PB84-200880

Wastes from Manufacture of Dyes and Pigments. Volume 2. Azo Dyes and Pigments (Excluding Benzidine and Its Congeners)

SRI International, Menlo Park, CA

Prepared for

Industrial Environmental Research Lab.-
Cincinnati, OH

Jun 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-200880

EPA-600/2-84-111b
June 1984

WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 2. AZO DYES AND PIGMENTS (Excluding Benzidine and Its Congeners)

By

D. C. Bomberger
R. L. Boughton

SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Contract 68-03-2944
Task 1, Subtask 2

Project Officer
Mark J. Stutsman
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-84-111b

2.

3. RECIPIENT'S ACCESSION NO. PB84 200880

4. TITLE AND SUBTITLE

WASTES FROM MANUFACTURE OF DYES AND PIGMENTS:
VOL. 2: AZO DYES AND PIGMENTS (EXCLUDING
BENZIDINE AND ITS CONGENERS)

5. REPORT DATE June 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) D.C. Bomberger & R.L. Boughton

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

SRI International
333 Ravenswood Ave.
Menlo Park, CA 94025

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO. 68-03-2944

12. SPONSORING AGENCY NAME AND ADDRESS

Industrial Environmental Research Laboratory
Office of Research & Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

In a study of the manufacture of azo dyes and pigments, several solid wastes that could contain hazardous material were identified. These solid wastes included filter cake from clarifying operations, wastewater treatment solids, intermediates on discarded shipping containers, and fines collected in baghouses used in grinding and drying operations. An aqueous waste stream containing process wastewater and mother liquor that could contain hazardous material was also identified. The major components in the solid and liquid streams were identified, and the amounts produced were estimated. These estimates were made on an individual dye basis and summarized on an industry-wide basis. The major potential discharges of dye, unreacted intermediates, and reaction by-products were in the mother liquor after dye or pigment transferred to wastewater treatment solids. Other major sources of solid residues included dye and pigments on baghouses fines, intermediate in discharged shipping containers, and filter cake solids. Pigments manufacture represented the most important source of wastes because of its large volume relative to dyes. The emissions showed that on an industry-wide basis 2-naphthol and 3-hydroxy-2-naphthoic acid account for nearly 50% of the intermediates estimated to be in the combined aqueous-solid stream [650 metric tons/year (mt/yr)]. This stream is also estimated to contain 350 mt/yr of dyes and pigments and 640 mt/yr of reaction byproducts on an industry-wide basis. The total amount of dye or pigment in the solid residue from azo dye and pigment manufacturing is estimated to be 550 mt/yr.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)* UNCLASSIFIED

20. SECURITY CLASS *(This page)* UNCLASSIFIED

21. NO. OF PAGES 215

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

In a study of the manufacture of azo dyes and pigments, several solid wastes that could contain hazardous material were identified. These solid wastes included filter cake from clarifying operations, wastewater treatment solids, intermediates on discarded shipping containers, and fines collected in baghouses used in grinding and drying operations. An aqueous waste stream containing process wastewater and mother liquor that could contain hazardous material was also identified.

The major components in the solid and liquid streams were identified, and the amounts produced were estimated. These estimates were made on an individual dye basis and summarized on an industry-wide basis. The major potential discharges of dye, unreacted intermediates, and reaction by-products were in the mother liquor after dye or pigment transferred to wastewater treatment solids. Other major sources of solid residues included dye and pigments on baghouses fines, intermediates in discarded shipping containers, and filter cake solids (which could contain unreacted intermediates, partially coupled dye molecules, and N-nitrosamines).

Pigment manufacture represented the most important source of wastes because of its large volume relative to dyes. The emissions estimates showed that on an industry-wide basis 2-naphthol and 3-hydroxy-2-naphthoic acid account for nearly 50% of the intermediates estimated to be in the combined aqueous-solid stream [650 metric tons/year (mt/yr)]. This stream is also estimated to contain 350 mt/yr of dyes and pigments and 640 mt/yr of reaction by-products on an industry-wide basis. The total amount of dye or pigment in the solid residue from azo dye and pigment manufacturing is estimated to be 550 mt/yr, which makes the dyes and pigments themselves the more significant synthetic organic component of the total solid residue. Sampling at six representative manufacturing is estimated to be 550 mt/yr, which makes the dyues and pigments themselves the more significant synthetic organic component of the total solid residue. Sampling a six representative manufacturing sites was recommended to determine actual waste composition and amount.

This report was submitted in fulfillment of Contract No. 68-03-2944 by SRI International under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period February 1981 to March 1982, and work was completed as of August 1983.

CONTENTS

FOREWORD.. iii

ABSTRACT.. iv

TABLES.. vi

1. INTRODUCTION... 1

2. SUMMARY AND CONCLUSIONS.................................. 22

3. PROCESS CHEMISTRY.. 24

   Introduction... 24
   Diazotization.. 25
   Coupling... 28
   Other Reactions.. 40
   Chemistry of Azoic Compounds............................. 43

4. DYE INTERMEDIATES.. 45

5. SOURCES OF WASTE DISCHARGES DURING AZO DYE AND PIGMENT MANUFACTURE.. 59

   Overview of Azo Dye and Pigment Production Processes...... 60
   Raw Material Receiving and Handling...................... 62
   Dye Synthesis.. 65
   Product Filtration....................................... 67
   Drying, Grinding, Standardization, Blending and Packaging.. 70
   Summary of Aqueous and Solid Waste Emission Estimates..... 71
   Wastewater Treatment..................................... 74

6. SOLID AND AQUEOUS WASTE PRODUCTION....................... 79

REFERENCES.. 194

APPENDICES

A. Example of Multistage Process for a Complex Dye........... 198
B. Estimation of By-Products and Unreacted Intermediates Produced by Dye and Pigment Manufacture.................. 202

TABLES

Number Page

1. Azo Dyes and Pigments Included in this Study.................... 2
2. Azo Dyes and Pigments for Which no Structure Information was Available.................... 16
3. Azoic Coupling Components and Azoic Diazo Components Included in this Study.................... 21
4. Colour Index Descriptions of Monazo Dye and Pigment Subclasses.................... 30
5. Colour Index Classification of the Azo Colouring Matters.......... 33
6. Colour Index Descriptions of the Disazo Dye and Pigment Subclasses.................... 34
7. Colour Index Descriptions of the Trisazo Dye and Pigment Subclasses.................... 37
8. Organic Intermediates and Other Chemicals used in Azo Dye and Pigment Manufacture for which Physical Property Data were Found.................... 46
9. Organic Intermediates for which no Physical Property Data were Found.................... 52
10. Summary of the Estimated Aqueous Wastes and Solid Residue Produced by Water Soluble Dye Manufacturing Operations........... 72
11. Summary of the Estimated Aqueous Waste and Solid Residue Produced by Pigment and Solvent and Disperse Dye Manufacturing Operations.................... 73
12. Estimated Wastes Produced in Manufacturing Azo Dyes and Pigments Other Than Those Based on Benzidine and Its Congeners.................... 82
13. Intermediates Used in Table 12 that have Common Names............ 170
14. Directory of Azo Dye and Organic Pigment Manufacturers, 1978..... 172
15. Producers of Monoazo Dyes and Pigments.................... 174
16. Producers of Disazo Dyes and Pigments.................... 184
17. Producers of Trisazo, Tetrakisazo and Polyazo Dyes and Pigments.................... 188
18. Producers of Azoic Diazo Components.................... 189

TABLES (Concluded)

19. Producers of Azoic Coupling Components.......................... 190

20. Estimated Total Quantity of Organic Intermediates in Solid and Aqueous-Solid Wastes from the Manufacture of Azo Dyes and Pigments other than Those Based on Benzidine and Its Congeners.................................... 191

B-1. Example Estimation of By-Products and Unreacted Intermediates from Production of Acid Black 1.................... 203

B-2. Results of By-Product Estimation from Azo Dye Synthesis.......... 205

SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes have been listed in regulations as being hazardous because of their chemical composition. The objective of this preliminary study is to help determine if wastes produced by the manufacture of dyes and pigments in the United States might require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing will be used to identify all wastes that may contain significant chemical hazards. An analysis of the industry will be used to determine specific manufacturers where the candidate wastes are produced. This information will help the U.S. Environmental Protection Agency, Office of Solid Wastes, to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes from the manufacture of azo dyes and pigments based on intermediates other than benzidine and its congeners.

Among the commonly recognized structural classes of dyes and pigments, the most important commercially in the United States are the azo dyes and pigments. The 1978 U.S. production of azo dyes and pigments was approximately 41,000 metric tons or about 35% of all U.S. dye and pigment production. These dyes and pigments are characterized by the presence of one or more azo groups (-N=N-) in the molecule. Consequently, the class can be divided into subclasses (monoazo, disazo, trisazo, tetrakisazo, and polyazo). A special subclass consists of azoic compounds; the azoic coupling components, azoic compositions, and azoic diazo components, that are reacted on the fiber to produce azo dyes. The azo dyes, pigments, and azoic compounds based on benzidine and its congeners were studied separately as described in another report. This study deals with the remaining azo dyes, pigments, and azoics.

The azo dyes and pigments produced in commercial quantities in the United States were selected as the subject of this study because of the current concerns about their possible adverse effects on the environment and human health. The Colour Index (The Society of Dyers and Colourists, 1980) numbers and names of the dyes and pigments for which chemical composition information was available are shown in Table 1. The dyes and pigments are listed in subgroups according to manufacturing chemistry. (These subgroups and the C.I. number ranges are described in Section 3.) The 1978 U.S. production levels of

Table 1

AZO DYES AND PIGMENTS INCLUDED IN THIS STUDY
(1978 Production Figures from the
U.S. International Trade Commission)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
Monoazo Dyes and Pigments			
11000-11435	11000	Solvent Yellow 1	> 2.3
	11005	Disperse Orange 3	21.4
	11014	Basic Red 30	> 2.3
	11021	Solvent Yellow 56	> 4.5
	11043	Basic Violet 18	> 2.3
	11052	Basic Blue 54	> 6.8
	11055	Basic Red 22	> 2.3
	11056	Basic Orange 24	> 2.3
	11077	Disperse Blue 165	> 6.8
	--	Disperse Blue 79	1284
	11085	Basic Red 18	147.3
	11087	Basic Yellow 15	> 2.3
	11100	Disperse Orange 5	> 4.5
	11110	Disperse Red 1	174.1
	11115	Disperse Red 13	> 6.8
	11116	Disperse Red 73	> 4.5
	11117	Disperse Red 90	> 2.3
	11119	Disperse Orange 30	> 6.8
	--	Disperse Red 54	> 4.5
	11150	Disperse Red 7	> 2.3
	11152	Disperse Brown 1	18.2
	11154	Basic Blue 41	> 4.5
	11160	Solvent Yellow 3	> 14[a]
	11210	Disperse Red 17	77.3
	11215	Disperse Red 5	36.4
	11227	Disperse Orange 25	325.5
	11228	Disperse Red 65	104.5
	11270	Basic Orange 2	283.6
	11320	Basic Orange 1	94.1
	11365	Disperse Black 1	> 5[a]

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
11440-11630	11460	Basic Red 29	> 5[a]
	11480	Basic Yellow 24	> 4.5
11640-11770	11660	Pigment Yellow 5	> 0.9
	11670	Pigment Yellow 6	> 0.5
	11680	Pigment Yellow 1	199.5
	11710	Pigment Yellow 3	66.4
	11720	Pigment Yellow 9	> 0.5
	11725	Pigment Orange 1	> 0.9
	11727	Pigment Yellow 98	> 0.5
	11730	Pigment Yellow 2	> 0.5
	11738	Pigment Yellow 73	245.5
	11740	Pigment Yellow 65	>50[a]
	11741	Pigment Yellow 74	588.2
	11765	Pigment Yellow 49	> 0.5
	11767	Pigment Yellow 97	> 0.5
	11770	Pigment Yellow 75	> 0.5
11800-11975	11855	Disperse Yellow 3	>95[a]
12050-12211	12055	Solvent Yellow 14	173.2
	12060	Pigment Orange 2	> 5[a]
	12070	Pigment Red 1	> 2.7
	12075	Pigment Orange 5	309.1
	12085	Pigment Red 4	49.5
	12090	Pigment Red 6	10.5
	12100	Solvent Orange 2	> 2.3
	12120	Pigment Red 3	485.9

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
12050-12211 (Continued)	12140	Solvent Orange 7	> 6.8
	12150	Solvent Red 1	> 2.3
	12156	Solvent Red 80	> 2.3
12300-12505	12300	Pigment Red 21	> 5[a]
	12310	Pigment Red 2	23.2
	12315	Pigment Red 22	35.5
	12320	Pigment Red 32	> 0.9
	12355	Pigment Red 23	200
	12360	Pigment Red 31	> 0.9
	12367	Pigment Orange 38	> 0.5
	12370	Pigment Red 112	> 0.9
	12390	Pigment Red 17	41.4
	12395	Pigment Red 13	> 0.9
	12420	Pigment Red 7	> 0.9
	12460	Pigment Red 9	>10[a]
	12465	Pigment Red 15	> 0.5
	12467	Pigment Red 188	> 0.5
	12475	Pigment Red 170	> 0.9
	12476	Disperse Red 220	> 2.3
	12480	Pigment Brown 1	> 0.5
	12485	Pigment Red 146	> 5[a]
	12490	Pigment Red 5	25.9
12600-12875	12700	Solvent Yellow 16	> 2.3
	12705	Pigment Yellow 60	> 0.9
	12715	Solvent Red 8	> 2.3
	12770	Disperse Yellow 4	> 2.3
	12775	Pigment Greeen 10	> 0.9

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
13010-13710	13025	Acid Orange 52	> 2.3
	13065	Acid Yellow 36	> 6.8
	13080	Acid Orange 5	> 2.3
	13091	Acid Orange 1	> 2.3
	13095	Acid Yellow 63	> 2.3
	13150	Acid Orange 50	> 2.3
	13190	Reactive Yellow 4	> 2.3
	13245	Reactive Yellow 3	> 2.3
	13250	Mordant Brown 33	> 4.5
	13265	Mordant Brown 70	> 2.3
	13361	Acid Green 35	> 2.3
	13390	Acid Blue 92	> 9[a]
13890-13970	13900	Acid Yellow 99	> 9.1
	13906	Acid Yellow 151	1620.9
	13950	Direct Yellow 27	> 2.3
13990-14155	14025	Mordant Yellow 1	> 2.3
	14030	Mordant Orange 1	> 4.5
	14110	Mordant Yellow 20	> 2.3
	14155	Direct Green 28	> 2.3
14160-14345	14170	Acid Yellow 65	> 4.5

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
14600-15085	14645	Mordant Black 11	> 45[a]
	14700	Food Red 1	> 4.5
	14710	Acid Red 4	19.5
	14720	Acid Red 14	> 25.5
	14830	Acid Red 20	> 0.5
	14880	Acid Blue 158	> 4.5
	15050	Acid Blue 158:1	> 4.5
15500-16315	15510	Acid Orange 7	206.8
	15575	Acid Orange 8	142.2
	15585	Pigment Red 53	1800
	15602	Pigment Orange 46	> 0.5
	15620	Acid Red 88	40.0
	15630	Pigment Red 49	3150
	15670	Mordant Violet 5	> 2.3
	15705	Mordant Black 17	> 4.5
	15711	Acid Black 52	406.8
	15800	Pigment Brown 5	> 1.8
	15825	Pigment Red 58	> 0.9
	15850	Pigment Red 57	1550
	15860	Pigment Red 52	798.6
	15865	Pigment Red 48	1135.5
	15880	Pigment Red 63	25.9
	15970	Acid Orange 12	> 2.3
	15985	Food Yellow 3	488.2
	16035	Food Red 17	867.3
	16105:1	Pigment Red 60:1	136.2
	16105	Mordant Red 9	> 2.3
	16150	Acid Red 26	> 2.3
	16185	Acid Red 27	> 2.3
	16230	Acid Orange 10	65.9
	16255	Acid Red 18	> 4.5

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
16500-16730	16580	Acid Violet 3	> 6.8
17000-17260	17025	Acid Violet 1	> 2.3
	17045	Acid Red 37	> 4.5
	17053	Acid Red 57	> 4.5
	17100	Acid Brown 90	> 2.3
	17101	Acid Red 266	> 9.1
	17200	Acid Red 33	> 4.5
	--	Acid Red 337	794.
17750-18245	17755	Acid Red 137	41.8
	17757	Reactive Orange 16	> 2.3
	17590	Mordant Brown 40	> 2.3
	17907	Reactive Orange 1	> 2.3
	17908	Reactive Red 8	> 2.3
	18050	Acid Red 1	154.1
	18055	Acid Violet 7	> 4.5
	18075	Acid Violet 12	> 2.3
	18097	Reactive Violet 5	> 2.3
	18158	Reactive Red 1	> 2.3
	18165	Acid Black 60	> 2.3
	18200	Reactive Red 2	> 4.5
18260-18270	18260	Reactive Orange 4	> 4.5
	18270	Reactive Orange 13	> 2.3

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
18670-19245	18690	Acid Yellow 121	> 2.3
	18732	Acid Orange 60	298.6
	18740	Acid Orange 72	> 2.3
	18745	Acid Orange 74	> 4.5
	18760	Mordant Red 7	> 9.1
	18810	Acid Red 186	> 2.3
	18820	Acid Yellow 11	> 2.3
	18821	Mordant Yellow 8	> 2.3
	18835	Acid Yellow 25	> 2.3
	18852	Reactive Yellow 17	> 2.3
	18890	Acid Yellow 34	> 4.5
	18900	Acid Yellow 29	> 2.3
	18930	Acid Yellow 200	> 2.3
	18950	Acid Yellow 40	> 6.8
	18965	Acid Yellow 17	84.1
	18967	Acid Yellow 19	> 9.1
	18971	Reactive Yellow 1	> 2.3
	18972	Reactive Yellow 2	> 2.3
	19005	Acid Yellow 127	> 2.3
	19010	Acid Yellow 54	> 4.5
	19140	Acid Yellow 23	730
19300-19610	19351	Acid Red 179	> 2.3
	19555	Direct Yellow 28	25.9

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
Disazo Dyes and Pigments			
Disazo Dyes I			
20000-20045	20040	Pigment Yellow 16	> 0.4
20070-20140	20110	Mordant Brown 1	> 4.5
20150-20305	20150	Mordant Brown 18	> 2.3
	20170	Acid Orange 24	> 13.6
	20177	Acid Brown 354	> 2.3
	20195	Acid Brown 14	106.4
	20250	Acid Brown 83	> 2.3
20310-20540	20460	Acid Blue 29	> 2.3
	20470	Acid Black 1	169.1
	20480	Acid Black 41	> 2.3
	20495	Acid Green 20	> 9.1
	20505	Reactive Black 5	> 2.3
Disazo Dyes II			
21000-21030			
	21000	Basic Brown 1	41.8
	21010	Basic Brown 4	110
	21030	Basic Brown 2	> 2.3

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Name	Production (mt/yr)
21230-21280	21230	Solvent Yellow 29	> 4.5
	21240	Solvent Yellow 30	> 2.3
	21250	Solvent Red 22	> 2.3
24750-24840	24810	Acid Red 134	> 2.3
24850-24920	24890	Direct Yellow 4	300.4
	24895	Direct Yellow 12	> 6.8
25080-25135	25100	Mordant Yellow 16	> 2.3
	25135	Acid Yellow 38	> 2.3
25200-25450	25200	Direct Orange 73	> 2.3
	25380	Direct Red 75	> 2.3
Disazo Dyes III			
26006-26150	26050	Solvent Red 19	> 2.3
	26070	Disperse Yellow 23	217.7
	26077	Disperse Orange 29	196.8
	26100	Solvent Red 23	> 2.3
	26105	Solvent Red 24	> 9.1
	26120	Solvent Red 26	> 4.5
	26125	Solvent Red 27	> 2.3
26200-26440	26360	Acid Blue 113	> 9[a]
	26370	Acid Black 24	> 2.3

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
26200-26440 (Continued)	26410	Acid Blue 118	> 2.3
	26440	Reactive Brown 1	> 2.3
26500-26580	26520	Mordant Orange 6	> 9.1
	26550	Acid Orange 51	> 2.3
26900-27311	26900	Acid Red 151	> 15.9
	26905	Acid Red 66	> 2.3
	27200	Acid Red 115	> 4.5[a]
	27290	Acid Red 73	74.5
	27291	Solvent Red 30	> 2.3
27600-27790	27680	Direct Red 16	> 4.5
27850-27990	27855	Direct Violet 7	> 2.3
	27885	Direct Violet 9	> 4.5
	27925	Direct Blue 67	> 2.3
28100-28500	28160	Direct Red 81	1066.4
	28255	Direct Orange 74	> 4.5[a]
Disazo Dyes IV			
29000-29090	29000	Direct Yellow 44	> 6.8
	29025	Direct Yellow 50	102.3
	29030	Direct Yellow 51	> 2.3

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
29000-29090 (Continued)	29042	Direct Yellow 118	> 2.3
	29058	Direct Orange 72	> 6.8
	29060	Direct Yellow 34	> 6.8
	29065	Direct Red 79	> 4.5
29100-29130	29100	Direct Red 31	> 4.5
	29105	Direct Violet 14	> 2.3
	29110	Direct Red 149	> 2.3
	29120	Direct Violet 66	> 4.5
29150-29232	29155	Direct Orange 29	> 2.3
	29156	Direct Orange 102	192.3
	29160	Direct Red 23	65.4
	29165	Direct Red 4	> 2.3
	29175	Direct Red 62	> 4.5
	29180	Direct Red 73	> 2.3
	29185	Direct Red 24	94.1
	29190	Direct Red 26	> 2.3
	29200	Direct Red 72	266.4
	29210	Direct Red 122	> 2.3
	29225	Direct Red 83	67.3

Table 1 (Continued)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
Trisazo Dyes and Pigments			
Trisazo I			
30000-30030	30015	Direct Black 78	> 2.3
Trisazo II			
31500-32055	31600	Direct Black 80	> 9.5[a]
Trisazo IV			
34005-34025	34010	Direct Blue 126	> 2.3
34040-34060	34045	Direct Green 26	> 2.3
34080-34100	34085	Direct Blue 120	> 4.5
	34090	Direct Blue 120A	> 4.5
34200-34230	34200	Direct Blue 78	> 2.3
	34220	Direct Blue 75	> 2.3
34260	34260	Direct Green 51	> 2.3

Table 1 (Concluded)

C.I. Subgroup	C.I. No.	C.I. Dye Name	Production (mt/yr)
Tetrakisazo Dyes and Pigments			
35000-35900	35005	Direct Brown 44	> 4.5[a]
	35255	Direct Black 19	> 2.3
	35435	Direct Black 22	> 11.4
	35780	Direct Red 80	200.9

---

[a] 1977 production range minimum from CICIS.

the marketed product (including inert salts and other material used to produce a standardized product) are also shown in this table. The data in this table were taken from the Organic Dyes and Pigments Data Base, which was prepared by SRI International (Swett, et al., 1983). For some dyes and pigments, production is shown only as greater than a minimum number. These are dyes and pigments produced by three or fewer manufacturers so that public sources do not list specific production amounts. The CICIS* data base lists production ranges for some of these dyes and pigments in its nonconfidential files. The production ranges cover an order of magnitude that does not always overlap the 1978 values derived from the U.S. International Trade Commission (1979) which was the basis of the production amounts in the Organic Dyes and Pigments Data Base. The CICIS values are shown in Table 1 when they exceeded the minimum U.S. International Trade Commission values. It is important to note that the CICIS production values are for the unstandardized material and do not include the inert ingredients used to standardize the product. In addition, production claimed confidential is not included. This means that, since Table 1 is based primarily on standardized products, the minimums for the CICIS production range values are definitely only a lower bound on production.

The azo dyes and pigments that have proprietary structures and that have not been assigned C.I. numbers by the Society of Dyers and Colourists (1980) are listed in Table 2. Because no information is available on the intermediates used to produce these dyes, no waste production estimates can be made; therefore, these dyes and pigments are not discussed in this report.

In 1972, the azoic compounds, shown in Table 3, accounted for about 4650 metric tons (mt) of product (U.S. Tariff Commission, 1975). The 1972 production of each subclass was as follows:

Azoic Compound	mt
Azoic diazo components	2180
Azoic coupling components	1320
Azoic compositions	1146

Because the compounds involved in producing these azoics are identical to intermediates that are used for dye synthesis, no waste production estimates were made for azoics.

In the following sections of this report the process chemistry of the azo dyes and pigments and the sources of waste during azo dye and pigment manufacture are discussed in detail. The final section gives the estimated amounts of solid and aqueous wastes produced during azo dye and pigment manufacture developed from the engineering analysis of Section 5.

---

*Chemicals in Commerce Information System (CICIS) (Nonconfidential files of the TSCA Inventory). U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington, D.C.

Table 2

AZO DYES AND PIGMENTS FOR WHICH NO STRUCTURE INFORMATION WAS AVAILABLE

Monoazo Dyes and Pigments

C.I. Acid Black 107
C.I. Acid Black 172
C.I. Acid Brown 31
C.I. Acid Brown 223
C.I. Acid Green 70
C.I. Acid Orange 64
C.I. Acid Orange 119
C.I. Acid Red 182
C.I. Acid Red 194
C.I. Acid Red 211
C.I. Acid Red 257
C.I. Acid Red 278
C.I. Acid Red 309
C.I. Acid Red 324
C.I. Acid Red 361
C.I. Acid Red 384
C.I. Acid Yellow 128
C.I. Acid Yellow 129
C.I. Acid Yellow 169
C.I. Acid Yellow 174
C.I. Acid Yellow 221

C.I. Basic Orange 26
C.I. Basic Orange 28
C.I. Basic Orange 31
C.I. Basic Orange 39
C.I. Basic Red 17
C.I. Basic Red 23
C.I. Basic Red 73
C.I. Basic Red 101

C.I. Direct Yellow 127
C.I. Direct Yellow 137
C.I. Direct Yellow 147
C.I. Disperse Blue 94
C.I. Disperse Blue 102
C.I. Disperse Blue 122
C.I. Disperse Blue 125
C.I. Disperse Blue 148
C.I. Disperse Blue 174
C.I. Disperse Blue 200
C.I. Disperse Blue 283
C.I. Disperse Blue 322
C.I. Disperse Brown 2
C.I. Disperse Brown 5
C.I. Disperse Orange 17
C.I. Disperse Orange 31
C.I. Disperse Orange 37
C.I. Disperse Orange 41
C.I. Disperse Orange 44
C.I. Disperse Orange 53
C.I. Disperse Orange 56
C.I. Disperse Orange 62
C.I. Disperse Orange 77
C.I. Disperse Orange 78
C.I. Disperse Orange 79
C.I. Disperse Orange 89
C.I. Disperse Orange 90
C.I. Disperse Orange 98
C.I. Disperse Orange 125
C.I. Disperse Red 30
C.I. Disperse Red 35

Table 2 (Continued)

Disazo Dyes and Pigments

C.I. Disperse Red 50
C.I. Disperse Red 76
C.I. Disperse Red 82
C.I. Disperse Red 88
C.I. Disperse Red 105
C.I. Disperse Red 106
C.I. Disperse Red 108
C.I. Disperse Red 109
C.I. Disperse Red 117
C.I. Disperse Red 135
C.I. Disperse Red 137
C.I. Disperse Red 140
C.I. Disperse Red 193
C.I. Disperse Red 271
C.I. Disperse Red 273
C.I. Disperse Red 316
C.I. Disperse Violet 33
C.I. Disperse Violet 40
C.I. Disperse Violet 43
C.I. Disperse Yellow 74
C.I. Disperse Yellow 136
C.I. Disperse Yellow 138
C.I. Disperse Yellow 148
C.I. Disperse Yellow 198

C.I. Mordant Brown 50
C.I. Mordant Orange 8

C.I. Reactive Blue 13
C.I. Reactive Brown 10
C.I. Reactive Orange 12
C.I. Reactive Orange 14
C.I. Reactive Orange 78
C.I. Reactive Red 5
C.I. Reactive Red 21
C.I. Reactive Red 29
C.I. Reactive Red 40
C.I. Reactive Red 41
C.I. Reactive Red 43
C.I. Reactive Red 49
C.I. Reactive Red 123
C.I. Reactive Yellow 6
C.I. Reactive Yellow 15
C.I. Reactive Yellow 18
C.I. Reactive Yellow 22
C.I. Reactive Yellow 24
C.I. Reactive Yellow 25
C.I. Reactive Yellow 27
C.I. Reactive Yellow 42

C.I. Solvent Red 210

Table 2 (Continued)

Disazo Dyes and Pigments (Continued)

C.I. Acid Yellow 159
C.I. Acid Yellow 219
C.I. Acid Orange 116
C.I. Acid Orange 128
C.I. Acid Orange 132
C.I. Acid Orange 152
C.I. Acid Orange 156
C.I. Acid Red 119
C.I. Acid Red 299
C.I. Acid Brown 158

C.I. Basic Yellow 83

C.I. Direct Yellow 84
C.I. Direct Yellow 107
C.I. Direct Yellow 132
C.I. Direct Yellow 139
C.I. Direct Orange 80
C.I. Direct Orange 118
C.I. Direct Red 236
C.I. Direct Red 238
C.I. Direct Red 239
C.I. Direct Blue 191
C.I. Direct Blue 260
C.I. Direct Blue 263
C.I. Direct Blue 279

C.I. Disperse Yellow 56
C.I. Disperse Orange 38
C.I. Disperse Orange 66
C.I. Disperse Orange 75
C.I. Disperse Red 161
C.I. Disperse Red 219
C.I. Disperse Blue 194

C.I. Pigment Yellow 93
C.I. Pigment Yellow 95
C.I. Pigment Yellow 126
C.I. Pigment Yellow 128
C.I. Pigment Orange 31
C.I. Pigment Red 144
C.I. Pigment Red 166
C.I. Pigment Red 220
C.I. Pigment Red 221
C.I. Pigment Brown 23

C.I. Reactive Blue 173
C.I. Reactive Brown 18
C.I. Reactive Black 9

C.I. Solvent Yellow 87
C.I. Solvent Red 33
C.I. Solvent Red 74
C.I. Solvent Red 164
C.I. Solvent Red 165

Table 2 (Continued)

Trisazo and Higher Azo Dyes and Pigments

C.I. Acid Yellow 59
C.I. Acid Yellow 114
C.I. Acid Yellow 135
C.I. Acid Yellow 199
C.I. Acid Yellow 216
C.I. Acid Orange 161
C.I. Acid Brown 97
C.I. Acid Brown 98
C.I. Acid Brown 239
C.I. Acid Black 29
C.I. Acid Black 92
C.I. Acid Black 194

C.I. Basic Yellow 41
C.I. Basic Orange 40
C.I. Basic Red 51
C.I. Basic Blue 76
C.I. Basic Blue 78

C.I. Direct Red 209
C.I. Direct Red 212
C.I. Direct Red 251
C.I. Direct Green 27
C.I. Direct Green 47
C.I. Direct Green 69

C.I. Disperse Yellow 96
C.I. Disperse Yellow 114
C.I. Disperse Yellow 126
C.I. Disperse Yellow 219
C.I. Disperse Orange 21
C.I. Disperse Orange 55
C.I. Disperse Orange 57
C.I. Disperse Orange 58
C.I. Disperse Orange 73
C.I. Disperse Orange 88
C.I. Disperse Orange 94
C.I. Disperse Orange 129
C.I. Disperse Orange 136
C.I. Disperse Red 118
C.I. Disperse Red 128
C.I. Disperse Red 136
C.I. Disperse Red 153
C.I. Disperse Red 163
C.I. Disperse Red 167
C.I. Disperse Red 177
C.I. Disperse Red 179
C.I. Disperse Red 195
C.I. Disperse Red 214
C.I. Disperse Red 274
C.I. Disperse Red 275
C.I. Disperse Red 278
C.I. Disperse Red 305
C.I. Disperse Red 309
C.I. Disperse Red 313
C.I. Disperse Red 319
C.I. Disperse Red 333
C.I. Disperse Violet 42
C.I. Disperse Violet 60
C.I. Disperse Blue 121
C.I. Disperse Blue 138
C.I. Disperse Blue 139

Table 2 (Concluded)

Trisazo and Higher Azo Dyes and Pigments (continued)

C.I. Disperse Blue 175
C.I. Disperse Blue 177
C.I. Disperse Blue 281
C.I. Disperse Blue 284
C.I. Disperse Blue 291
C.I. Disperse Blue 317
C.I. Disperse Green 9
C.I. Disperse Brown 10
C.I. Disperse Brown 18
C.I. Disperse Black 9
C.I. Disperse Black 33

C.I. Reactive Yellow 7
C.I. Reactive Yellow 86
C.I. Reactive Yellow 132
C.I. Reactive Yellow 133
C.I. Reactive Yellow 135
C.I. Reactive Orange 64
C.I. Reactive Orange 70
C.I. Reactive Orange 84
C.I. Reactive Orange 86
C.I. Reactive Red 11
C.I. Reactive Red 31
C.I. Reactive Red 33
C.I. Reactive Red 58
C.I. Reactive Red 120
C.I. Reactive Violet 1
C.I. Reactive Blue 89
C.I. Reactive Blue 109
C.I. Reactive Brown 17

C.I. Solvent Yellow 13
C.I. Solvent Yellow 71
C.I. Solvent Yellow 72
C.I. Solvent Orange 20
C.I. Solvent Orange 73
C.I. Solvent Orange 74
C.I. Solvent Red 105
C.I. Solvent Red 173

Table 3

AZOIC COUPLING COMPONENTS AND AZOIC DIAZO COMPONENTS INCLUDED IN THIS STUDY

C.I. No.	Azoic Diazo Component	Production (mt/yr)	C.I. No.	Azoic Coupling Component	Production (mt/yr)
37000	44	>2.3	37505	2	>2.3
37010	3	>4.5	37510	10	>2.3
37025	6	>2.3	37515	17	>2.3
37040	9	>6.8	37520	18	>4.5
37050	49	>2.3	37525	8	>2.3
37085	11	>2.3	37526	21	>4.5
37096	32	>2.3	37527	29	>4.5
37100	34	>2.3	37530	20	>4.5
37105	12	>2.3	37531	34	>4.5
37110	8	>4.5	37535	11	>4.5
37120	10	>6.8	37545	19	>2.3
37125	5	>6.8	37550	12	>2.3
37130	13	>6.8	37558	14	>4.5
37135	1	>6.8	37565	7	>4.5
37150	42	>2.3	37600	15	>2.3
37151	14	>2.3	37615	35	>2.3
37175	20	>2.3	--	43	>4.5

SECTION 2

SUMMARY AND CONCLUSIONS

In this preliminary study of azo dyes and pigments, the following solid residues were identified that might contain hazardous material:

- Filter cake from clarifying operation after diatozation and/or coupling. The cake could contain unreacted intermediates, partially coupled dye molecules, and N-nitrosamines. If the filter cake is treated with hypochlorite, as is the case at some plants, the total amount of organic material may be reduced, but additional chlorinated aromatics may be created. There was not enough information available to quantify this residue.
- Discarded shipping containers. These would be paper bags and fiber drums used to transport dye and pigment intermediates, and would contain a residual amount of intermediate when emptied.
- Wastewater treatment solids. The evidence suggests that the solids will be contaminated with low levels of all of the dye and pigment intermediates as well as the dyes and pigments themselves and some reaction by-products. If these solids are placed in a landfill, intermediates may be released as a result of reduction of the azo linkages under the anaerobic conditions prevailing in the landfill.
- Baghouse fines. The fines are generated during the drying, standardizing, and packaging of the dyes and pigments. The fines will be principally the dyes and pigments and inert salts. Anaerobic conditions in a disposal site could cause intermediates to be released from these fines.

On an industry-wide basis, the major sources of waste emissions are associated with azo pigment manufacture rather than dye manufacture simply because pigments are the major products produced. At any given plant, the major source of discharges of organic chemicals is probably the process wastewater rather than the solid residue stream since, at many locations, the process wastewater includes the mother liquor that contains unreacted intermediates and by-products in potentially high concentration. Actual emissions will, however, be quite site-specific, because emissions will be affected by the disposition of the mother liquor, specific treatment of individual process step wastewaters, the overall wastewater treatment system, and the treatment of the filter cakes. The intermediate, by-product, and dye and pigment emissions that were summarized in Section 6 (Tables 12 and 20) ignored these site-specific factors.

The information on the production patterns for dyes and pigments contained in Section 6 (Tables 12 and 15 through 19) was analyzed to choose representative manufacturers where a sampling program might be conducted to confirm the composition and the magnitude of the estimated waste emissions. Companies that manufacture the major volume azo dyes and pigments were recommended. There was no way, using public sources, to determine exactly how much of each dye or pigment was made at each manufacturing site; therefore it was assumed that each company producing a major dye or pigment produced a significant fraction of the total amount produced. The six companies are the American Color and Chemical Corp., American Cyanamid Co., Atlantic Chemical Corp., E. I. DuPont de Nemours & Co., Inc., Harshaw Chemical Co., and Toms River Chemical Corp.

The six companies that are recommended for a sampling program should yield samples from facilities using different manufacturing and waste treatment practices. Since there is considerable overlap in the actual dyes or pigments that they make, the six-company sampling program increases the chances of identifying material in the waste streams that may be sensitive to plant practices.

SECTION 3

PROCESS CHEMISTRY

INTRODUCTION

A discussion of the process steps required to synthesize the azo dyes and pigments will aid in formulating the emission estimates developed in Section 5. The first part of this section describes the azo dyes and pigments use classes as background. The remainder of this section is devoted largely to a discussion of the process chemistry of the two key steps required to synthesize these dyes and pigments, diazotization and coupling, with special attention given to the starting materials, intermediates, reaction conditions, and potential by-products. The recipe for an azo dye is shown in detail in Appendix A. Some azo dyes and pigments are produced by reactions other than diazotization and coupling, and these reactions are briefly discussed.

The majority of the commercially produced azo dyes and pigments considered in this report fall into the following classes:

- Direct dyes
- Acid dyes
- Disperse dyes
- Reactive dyes
- Solvent dyes
- Pigments.

In addition, small amounts of azoic components (azoic coupling components, azoic diazo components, and azoic compositions) are produced.

The class of direct dyes consists of anionic dyes substantive to cellulose when applied from an aqueous bath containing an electrolyte. Chemically, the azo direct dyes are mostly di-, tri-, and polyazo compounds, with only a few monazo compounds.

Acid dyes are water-soluble anionic dyes applied to nitrogeneous fibers (e.g., wool, silk, nylon, and modified acrylics) that function by virtue of the presence of one or more sulfonic acid or other acidic groups in the molecule.

Disperse dyes have been specially developed to dye cellulose acetate and some of the synthetic fibers. The class may be broadly divided into two general groups: insoluble simple azo dyes and insoluble aminoanthraquinone dyes (the anthraquinone dyes are discussed in a separate report). Both are highly dispersed and capable of penetrating fibers, and both general groups usually contain the ethanolamine side chain, $-NHCH_2CH_2OH$, or a similar group to increase dispersibility in water.

Reactive dyes, which link chemically to cellulosic fibers, are water-soluble compounds that contain reactive groups capable of combining with the hydroxyl groups of cellulose under alkaline conditions. The wet-fastness properties of these dyeings is high.

Solvent, or spirit-soluble, dyes are frequently simple azos used to color oils, waxes, varnishes, shoe dressings, lipsticks, and gasoline.

Included in organic pigments are substances (usually soluble in organic solvents) that impart a positive color to another substance (as opposed to whiting agents, extenders, and fillers).

The class of azoic compounds includes those materials used to produce insoluble azo dyes in-situ, usually on a textile substrate. This class consists of three subclasses: the azoic diazo components, the azoic coupling components, and the azoic compositions, which are mechanical mixtures of the first two in which the azoic diazo component has been stabilized to prevent coupling before application. The azoic diazo components consist of diazonium salts (or their parent amines when the dyer performs the diazotization) based on aromatic amines. Any primary aromatic amine that is capable of diazotization and coupling and that is free from sulfonic and other solublizing groups may, in principle, be used as an azoic diazo component, but the number of amines actually used is limited to about 50. The azoic coupling components are principally beta-naphthol derivatives, but also include arylamides. The anilide of beta-naphthol carboxylic acid is the most frequently used.

DIAZOTIZATION

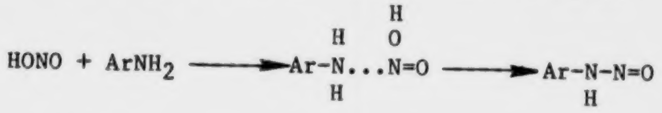
As applied in dye chemistry, diazotization is the conversion of an aromatic amine to the corresponding diazonium chloride using nitrous acid:[*]

$$\underset{\substack{\text{Aromatic}\\ \text{amine}}}{ArNH_2} + NaNO_2 + 2HCl \longrightarrow \underset{\substack{\text{Diazonium}\\ \text{chloride}}}{ArN{=}\overset{+}{N}Cl^{-}} + NaCl + 2H_2O$$

---

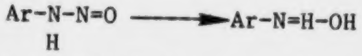
[*] Since nitrous acid is unstable, it is produced as needed from the reaction of aqueous solutions of sodium nitrite and hydrochloric acid at 0°C.

The mechanism of the diazotization reaction was elucidated by Hughes et al. (1958). Nitrous acid reacts with the primary amine by attachment of the nitroso group to the nitrogen with the elimination of water:



$$HONO + ArNH_2 \longrightarrow Ar\text{-}\underset{H}{\overset{H}{N}}...\overset{\overset{H}{O}}{N}\text{=}O \longrightarrow Ar\text{-}\underset{H}{N}\text{-}N\text{=}O$$

The product is unstable and isomerizes to a diazotic acid:



$$Ar\text{-}\underset{H}{N}\text{-}N\text{=}O \longrightarrow Ar\text{-}N\text{=}H\text{-}OH$$

The diazotic acid is also unstable in neutral or acid solution and usually decomposes rapidly to a diazonium salt:

$$Ar\text{-}N\text{=}N\text{-}OH \xrightarrow{HCl} Ar\text{-}N\text{=}N^+Cl^- + H_2O$$

When diazotization is applied to diamines such as m-phenylenediamine, both amino groups are diazotized, so the process, termed tetrazotization, produces a tetrazonium chloride.

$$2\ HONO + H_2N\text{-}Ar\text{-}NH_2 \xrightarrow{HCl} Cl^{-+}N\text{=}N\text{-}Ar\text{-}N\text{=}N^+Cl^-$$

The azotization reaction is generally conducted at 0° to 5°C (to retard decomposition of the diazonium salts formed) for one to three hours using a molar ratio of diamine:sodium nitrite:hydrochloric acid of 1:1:2.5. The reaction product is an aqueous solution containing approximately 15 wt% of the diazotized material and 7 wt% sodium chloride.

Sodium nitrite is employed in the theoretical quantity, but excess acid must be used to prevent partial diazotization and condensation of the diazonium salt with the undiazotized amine to form the diazoamino compound.

$$Ar\text{-}N\text{=}N\text{-}Ar\text{-}NH_2$$

Excess mineral acid also stablizes the diazonium salt by inhibition of decomposition due to other secondary reactions (Venkataraman, 1952).

The diazotization reportedly gives high yields (Abrahart, 1968; Lubs, 1955), so very little of the starting amine is believed to be left in the reaction product. However, some undecomposed diazotic acid (Ar-N=N-OH) may be present. In addition to the diazoamine by-products mentioned above, one source (Roberts and Caserio, 1964) has indicated that the use of hydrochloric acid may result in the formation of aryl chlorides as a result of the decomposition of the diazonium salt to nitrogen gas and a carbonium ion and reaction of the latter with chloride ion:

$$Ar\text{-}N\text{=}N^+Cl^- \longrightarrow N_2 + Ar^+ + Cl^- \longrightarrow ArCl$$

The aryl chlorides are considered "terminated" by-products because they cannot be converted to the desired azo compounds in subsequent coupling steps. They are not completely inert, however, and may react with the original primary amine starting material to form secondary amines, which in turn, may be converted by the nitrous acid to their N-nitroso derivatives (Rys and Zollinger, 1972):

$$\mathrm{ArCl + ArNH_2 \xrightarrow{H^+} HCl + Ar_2NH \xrightarrow{HONO} Ar_2N{-}N{=}O}$$

N-nitrosamines are very weak bases and are characteristically yellow or orange-yellow insoluble liquids or solids that separate from solution. If an N-nitroso compound is formed during a diazotization reaction, the liquor may require clarification by filtration before transfer to the coupling reactor. This operation may be done only as required, although clarification is specifically called for in some dye recipes (BIOS, 1945)

Free aryl radicals formed during breakdown of diazonium salts to yield nitrogen gas may react with (among others) diazonium cations with formation of a symmetrical azo compound Ar-N=N-Ar or the radicals may attack undecomposed covalent diazo compounds with formation of a diazo biaryl compound, Ar-Ar-$N{=}N^+Cl^-$, which eventually yields polyaryls or combines to form an arylazobiaryl, Ar-Ar-N=N-Ar (Saunders and Waters, 1946).

Snow (1932) measured the rate of decomposition of diazonium chlorides based on various amines at 20°C and has arranged them in the following order of decreasing stability:

p-Chloroaniline
m-Nitroaniline
1-Amino-2,4-dimethyl-6-nitrobenzene
o-Nitroaniline
o-Anisidine
p-Nitroaniline
p-Phenetidine
5-Aminosalicylic acid
p-Toluidine
Aminoazobenzene
p-Aminophenol
p-Phenylenediamine (diazotized)
Picramic acid
Sulfanilic acid
p-Aminobenzoic acid
α-Naphthylamine
p-Anisidine
β-Naphthylamine
1-Amino-2,4-dimethylbenzene
Anthranilic acid
Aminoazotoluene
m-Aminobenzoic acid
1-Amino-3,4-dimethylbenzene
1-Amino-2,3-dimethylbenzene
Aniline
o-Toluidine
m-Toluidine
m-Anisidine
1-Amino-2,6-dimethylbenzene
p-Phenylenediamine (tetrazotized)

Electronegative substitution of the amine increases the stability of the diazonium salt. Substitution by chlorine, carboxyl, sulfonic, or nitro groups and by methyl, hydroxyl, methoxy, or phenyl groups may increase the stability of the diazonium salt (Crossley et al., 1940). Diazonium sulfates are more stable and the acetates less stable than the chlorides.

COUPLING

As applied in azo dye manufacture, coupling is the conversion of a diazonium salt (the diazo component) to an azo compound by reaction with an aromatic compound (the coupling component), which generally has a strong electron-donating substituent on the aromatic ring (e.g., a phenolic, amino, or substituted amino group):

$$\underset{\text{Diazo Component}}{Ar\text{-}N{=}\overset{+}{N}Cl^{-}} + \underset{\text{Coupling Component}}{A'\text{-}H} \longrightarrow \underset{\text{Azo Compound}}{AR\text{-}N{=}N\text{-}Ar'} + HCl$$

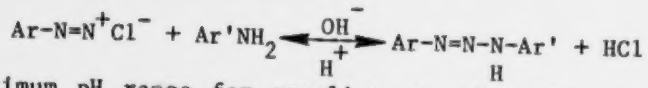
For the tetrazonium chlorides made from diamines, the initial desired reaction may be either coupling of both diazonium chlorides or coupling of only one. In the latter case, the resultant product may be coupled again with a different coupling component. The final products from the two different procedures are the symmetrical and unsymmetrical disazo compounds.

$$Ar'\text{-}N{=}N\text{-}Ar\text{-}N{=}N\text{-}Ar' \qquad\qquad Ar'\text{-}N{=}N\text{-}Ar\text{-}N{=}N\text{-}Ar''$$

A variety of coupling components are used to produce the commercially significant azo dyes and pigments. The specific chemicals used for each of the azo dyes and pigments included in this study are enumerated in Section 6. The structures of the coupling components used depend on the color desired and the type of dye desired. For direct and acid dyes, the molecules contain solubilizing groups such as hydroxyl, sulfonic acid, or carboxylic acid groups, whereas for pigments and for solvent and disperse dyes these groups are usually absent. The direct dye molecule is designed to be long and have aromatic components that are coplanar, whereas the acid dye molecule is more compact.

The structure of the coupling component has a complex effect on the rate of the coupling reaction and the products formed. In general, the phenols couple very readily in alkaline media at both their ortho and para positions. If excess diazo component is present, multiple couplings are possible and di- and triazo phenols may result. The anilines couple less readily than the phenols and only in the para position. Both coupling of phenols and anilines is impeded by electron-attracting substituents (e.g., nitro, sulfonic) and facilitated by electron-donating substituents (e.g., methyl, methoxy).

The structure of the diazonium salt also affects the rate of the coupling reaction and the formation of by-products. In general, diazonium salts of negatively substituted amines, such as nitroanilines, nitrochloroanilines, and the aniline sulfonic acids, couple rapidly. Coupling is generally conducted under mildly alkaline conditions at 0°C to 5°C for 4 to 24 hours, using almost a 1:1 molar ratio of diazonium salt to coupling component. Coupling reactions are performed in a medium in which the equilibria of the diazo and the coupling component lies as far as possible toward the coupled product and where the coupling rates are fast. The rate of the coupling reaction of amines, for example, increases with increasing pH. However, a lower pH is used to suppress the decomposition of the diazonium compound and to suppress the formation of triazene compounds.



$$\text{Ar-N=N}^+\text{Cl}^- + \text{Ar'NH}_2 \underset{\text{H}^+}{\overset{\text{OH}^-}{\rightleftharpoons}} \text{Ar-N=N-}\underset{\text{H}}{\text{N}}\text{-Ar'} + \text{HCl}$$

There is an optimum pH range for coupling reactions for each combination of diazo and coupling components. This range is about pH 4 to 9 for anilines and other aromatic amines, 7 to 9 for enols, and 8.5 to 9.5 for phenols. The pH is commonly adjusted using soda ash so that the hydrochloric acid by-product from the coupling is converted to sodium chloride.

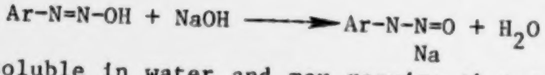
At the temperatures used for coupling, the reaction is reported to give good yields (90%-99%) of the desired azo compound (Rys and Zollinger, 1972; Lubs, 1955). However, because of side reactions that occur during diazotization (such as decomposition reactions), impurities may already be present in the diazonium chloride that decrease the overall apparent yield, and these impurities may also react to form additional side products.

If the diazonium chloride decomposes to nitrogen gas and a carbonium ion before the coupling reaction takes place (in the basic medium), the carbonium ion may react with hydroxyl ion to form phenols:

$$\text{Ar-N=N}^+\text{Cl}^- \longrightarrow \text{N}_2 + (\text{Ar}^+ + \text{Cl}^-) \xrightarrow{\text{NaOH}} \text{ArOH} + \text{NaCl}$$

These phenols are considered "terminated" by-products because they cannot be converted to the desired azo compounds and may occur during any step of the dye synthesis.

Any diazotic acid formed in the diazotization step that does not decompose to the desired diazonium chloride may react in the basic solution used for most coupling reactions to form stable diazotate salts:



$$\text{Ar-N=N-OH} + \text{NaOH} \longrightarrow \text{Ar-}\underset{\text{Na}}{\text{N}}\text{-N=O} + \text{H}_2\text{O}$$

These salts are insoluble in water and may require that the coupling reaction liquor be clarified by filtration before proceeding to the next process.

Table 4 shows the Colour Index descriptions of the monoazo dye and pigment subclasses. The subclasses are arranged in two sections consisting of dyes essentially insoluble in water and dyes soluble in water, respectively. Within each section the items are arranged in a succession based on the coupling component. Also shown in Table 4 are the number of dyes included in this study and the cumulative approximate U.S. production for each subclass.

Table 4

COLOUR INDEX DESCRIPTIONS OF MONAZO DYE AND PIGMENT SUBCLASSES

C.I. Numbers	Nature of Coupling Components	Major Application	Number of Dyes[a] Included in this Study	Approximate 1978 U.S. Production (mt)[b]	Subclass Average % Mole Excess[c]
Water-Insoluble Dyes (dyes without -COOH, -SO_3H, or SO_2NH_2 groups)					
11000-11435	Arylamines	Solvent and disperse	30	2638	7 cc
11440-11630	--	--	2	7	8 cc
11640-11770	Acetoacetyl compounds	Pigment	14	1106	4 cc
11800-11975	Phenols	Mordant, disperse, and solvent	1	14	
12000-12020	1-Naphthol	Solvent	0	—	—
12050-12211	2-Naphthol	Pigment and solvent	11	1046	8 cc
12300-12505	3-Hydroxy-2-naphthanilides	Pigment	19	339	10 cc
12600-12825	Heterocyclic hydroxy compounds	Disperse, pigment, and solvent	5	9	—
Water-Soluble Dyes (dyes with -COOH, SO_3H, or SO_2NH_2 groups)					
13000-13001	Dyes without auxochromic groups	Acid	0	—	—
13010-13710	Arylamines	Acid and mordant	12	36	3 azo
13890-13970	Acetoacetarylamides	Direct	3	1632	9 cc
13990-14155	Salicylic acid	Mordant	4	11	3 cc
14160-14345	Other phenol derivatives	Acid and mordant	1	4	—
14600-15085	1-Naphthol and 1-naphthol sulfonic acids	Acid and mordant	6	59	10 cc
15500-16315	2-Naphthol and 2-naphthol sulfonic acids	Acid and mordant	23	10837	5 cc
16500-16730	Naphthalenediols and dihydroxynaphthalene sulfonic acids	Acid and mordant	1	7	—
17000-17260	Aminonaphthol sulfonic acids	Acid	7	821	4 cc
17500-17670	N-alkyl(or aryl)aminonaphthol sulfonic acids	Mordant	0	—	—

Table 4 (Concluded)

C.I. Number	Nature of Coupling Components	Major Application	Number of Dyes[a] Included In This Study	Approximate 1978 U.S. Production (mt)[b]	Subclass Average % Mole Excess[c]
Water-Soluble Dyes (dyes with -COOH, SO_3H, or SO_2NH_2 groups) (Continued)					
17750-18245	Acylaminonaphtholsulfonic acids	Direct	12	223	
18260-18270	--		2	7	
18670-19245	Pyrazolones	Acid and mordant	21	1179	6 cc
19300-19610	Other heterocyclic hydroxy compounds	Acid, mordant, and direct	2	28	6 cc
Total[d]			172	20,000	

---

[a] For which CI numbers are available.

[b] Many production values are reported as a lower limit; thus the subclass production values are approximate.

[c] cc = coupling component added in excess; azo = azo component added in excess.

[d] Rounded.

A review of dye recipes given in the BIOS reports (1945) shows that in many cases excess ingredients are called for. The amount of excess ingredients used in the synthesis of a dye or pigment is used to estimate the losses of intermediates during dye manufacture (Section 5).

The BIOS recipes found for the monoazo dyes and pigments (49 with recipes out of 172 dyes and pigments with known ingredients included in this study) were used to calculate the molar addition of the coupling component and diazo component for each batch of dye produced. These values were then compared to find the molar excess of component added (if any). These excess amounts ranged from 12% excess diazo component (Pigment Orange 1, C.I. 11725) to 20% excess coupling component (Disperse Orange 3, C.I. 11100) based on the amine. Using the classification scheme for monazo dyes and pigments from the Colour Index (The Society of Dyers and Colourists, 1980), we compared these excess addition values on a subclass basis to see if dyes based on different components required common amounts of excess components. The subclass averages appear in Table 4. The majority of the subclasses show the addition of excess coupling components ranging from about 3 to 10%. However, many of the subclasses did not have enough recipes to give confidence that the pattern has been identified properly. Table 4 shows that subclass C.I. 15500-16315, derived from 2-naphthol (and 2-naphthol sulfonic acids) as coupling components, is estimated to account for approximately 54% of the estimated production of the monoazo dyes and pigments for which information was available. Within this subclass the top two pigments account for approximately 25% of the entire production estimated for monoazo class. The average value for this subclass of 5% excess coupling component should then have a major influence on the entire monoazo class average. This was indeed found to be the case since the entire monoazo class average was about 5% excess coupling component from the information available.

Table 5 summarizes the Colour Index classification scheme for disazo, trisazo, and the higher azo dyes. The table also indicates schematically the type of coupling reactions used to generate the dyes in each subclass. These reactions and the by-product formation in each subclass are discussed in more detail below.

Table 6 shows more of the details of the subclassification scheme for disazo dyes, in particular identifying the specific type of coupling components used and the nature of the azo product. The excess ingredients required in each subclasss were estimated from the BIOS recipes. The resulting estimates are not definitive because only 12 recipes were found, although there are 75 dyes in this class with known intermediates.

The Disazo I subclass is characterized by the coupling of two diazotized arylamines (often dissimilar) to a single coupling component. Several recipes called for excess diazo component of 3 to 8%, whereas others were stoichiometric. No recipes called for excess coupling components.

The Disazo II subclass is characterized by the use of a diamine that is tetrazotized and coupled to two coupling components (often dissimilar). Recipes found for this subclass called for addition of 0 to 10% excess coupling component based on the amine.

Table 5

COLOUR INDEX CLASSIFICATION OF THE AZO COLOURING MATTERS

Class of Azo Compound	General[a] Formula	C.I. Range
Disazo I	$A \rightarrow Z \leftarrow A'$	20000-20999
II	$E \leftarrow D \rightarrow E'$	21000-25999
III	$A \rightarrow M \rightarrow E$	26000-28999
IV	$A \rightarrow Z \cdot X \cdot Z \leftarrow A'$	29000-29999
Trisazo I	$E \leftarrow D \rightarrow Z \leftarrow A$	30000-31499
II	$E \leftarrow D \rightarrow M \rightarrow E'$	31500-33499
III	$A \rightarrow Z \leftarrow M \leftarrow A'$	33500-33999
IV	$A \rightarrow M \rightarrow M' \rightarrow E$	34000-34899
V	$A \rightarrow Z \begin{matrix} \leftarrow A' \\ \leftarrow A'' \end{matrix}$	34900-34999
Tetrakisazo and higher polyazo	Extensions of above	35000-36999

---

[a] Symbol key:

- A, a diazo component
- D, a tetrazo component
- E, a coupling component end group
- M, an amine that can be diazotized after coupling with a diazo component
- Z, a coupling component that can be coupled with two (or more) molecules of a diazo component (often dissimilar)
- **Z·X·Z, a binuclear coupling component capable of** coupling with two molecules of a diazo component(s)
- →, diazotized and coupled with

Table 6

COLOUR INDEX DESCRIPTIONS OF THE DISAZO DYE AND PIGMENT SUBCLASSES

C.I. Number	Nature of Coupling Component	Major Application	Number of Dyes[a] Included in This Study	Approximate 1978 U.S. Production (mt)[b]
Disazo I (general formula A→Z←A)				
20000-20045	Dyes without COOH, SO_3H or SO_2NH_2 salt-forming groups	Various	1	0.4
20070-20140	m-Arylenediamines	Acid and mordant	1	4.5
20150-20305	Phenol, resorcinol and 1-naphthol	Acid and mordant	5	126.9
20320-20540	Aminonaphthol sulfonic acid	Acid and mordant	5	185.1
			Subtotal	317

C.I. Number	Nature of Tetrazotisable Diamine	Major Application	Number of Dyes[a] Included in this Study	Approximate U.S. Production (mt)[b]
Disazo II (general formula B←D→E')				
Water-Insoluble Dyes (dyes without COOH, SO_3H, or SO_2NH_2 groups)				
21000-21030	m-Arylenediamines	Basic and solvent	3	154.6
21050-21220	Benzidine and derivatives[c]	Pigment	0	—
21230-21280	Diamines	Solvent	3	9.1
Water-Soluble Dyes (dyes with COOH, SO_3H, or SO_2NH_2 groups)				
21500-21725	Arylenediamines	Direct	0	—
22000-24500	Benzidine and derivatives[c]	Direct, acid, and mordant	0	—
24550-24565	(4,4′-Diamino-3,3′-biphenylene-dioxy) diacetic acid	Direct	0	—
24750-25735	Binuclear diamines	Direct	7	317
			Subtotal	496

Table 6 (Concluded)

C.I. Number	Nature of Second Coupling Component	Major Application	Number of Days Included in This Study[a]		Approximate 1978 U.S. Production (mt)[b]
Disazo III (general formula $A \rightarrow M \leftarrow E$)					
Water-Insoluble Dyes (dyes without COOH, SO_3H, or SO_2NH_2 groups)					
26000-26150	Various	Disperse and solvent	7		431
Water-Soluble Dyes (dyes with COOH, SO_3H, or SO_2NH_2 groups)					
26200-26440	Arylamines	Acid and direct	4		11.4
26500-26580	Phenol, resorcinol, or derivatives	Mordant and direct	2		11.4
26650-26785	1-Naphtholsulfonic acid	Acid and direct	0		—
26900-27311	2-Naphthol or 2-naphtholsulfonic acid	Acid and direct	5		97.3
27500-27560	Dihydroxynaphthalene sulfonic acid	Acid	0		—
27600-27790	Aminonaphthol sulfonic acid	Direct	1		4.5
27850-27990	Arylaminonaphthols	Direct	3		9.1
28100-28500	Acylamino (or aroylamino) naphthol sulfonic acids	Direct	2		1068.7
28650-28725	Pyrazolone or heterocyclic compounds	Direct	0		—
				Subtotal	1633
Disazo IV (general formula $A \rightarrow Z \cdot X \cdot Z \leftarrow A'$)					
29000-29090	Diphenylurea residue from phosgenation of simple aminoazo compound	Direct	7		131.8
29100-29130	6,6′ Iminobis-1-naphthol-3-sulfonic acid		4		13.6
29150-29232	6,6′-Ureylenebis-1-naphthol-3-sulfonic acid		11		701.5
29250-29275	Bis ureas or amides from diamines		0		—
29290-29295	Diphenylurea from phosgenation of aminophenylpyrazolone azo dye		0		—
				Subtotal	847
				Total	3293

---

[a] For which C.I. numbers were available.

[b] Many production values are reported as lower limits; thus the subclass production values are approximate.

[c] Azo dyes and pigments based on benzidine and its derivatives are not included in this study.

The Disazo III subclass, which is characterized by successive diazotization and coupling steps, accounts for about 50% of the total estimated disazo dye and pigment production. Three of the available recipes for this subclass called for no excess components. This included the largest volume disazo dye (Direct Red 81;C.I.28160), which accounted for about 30% of the total estimated production volume for the disazo class.

The majority of the dyes in the Disazo IV subclass are formed by treating 2 moles of an aminoazo compound with phosgene, producing a twice coupled binuclear component. No BIOS recipes were found for this subclass.

From the limited number of recipes available for the disazo class it is difficult to find an average value for excess components added. The 5% figure may, in many cases, overestimate the excess value; however, because the total estimated disazo class production is small compared with the monoazo class, a value of 5% excess coupling component is assumed for each coupling step.

Table 7 shows the details of the subclassification scheme for trisazo dyes, identifying the type of coupling component used and the nature of the azo product. Because of the coupling sequence and types of coupling components used, none of these is likely to be the homogeneous product indicated. The polyazo dyes must, in many cases, be mixed products and the dye structure given by the Colour Index represents no more than a probable major component. Only one BIOS recipe was found for the 13 tris and higher azo dyes and pigments with known intermediates that are included in this study. It is therefore difficult to assign an excess ingredient value. However, because these classes are small compared with the monoazo dye class, a value of 5% excess coupling component has been assumed during dye or pigment synthesis.

Because of the many azo dyes for which no recipes were found (197), the choice of 5% excess could be in error on a basis of the number of azo dyes studied (259). However, the individual dye recipes of the four monoazo pigments with the highest estimated production volume (Pigment Red 53, 49, 57, and 48), which together account for 36% of the estimated total monoazo dye production volume, called for 3, 7, 4, and 6% excess coupling component, respectively. The large fraction of the estimated total azo dye production that has approximately 5% excess coupling components called for in the BIOS recipes leads to the conclusion that the entire azo class may be represented by this value of 5%.

The reactions that yield undesirable couplings and by-products have different impacts on the waste produced when dyes and pigments in the various subgroups are synthesized. These differences are discussed below.

The monazo class should be the "cleanest" with respect to by-products because only one diazo compound is used and only one coupling reaction is required. For the most part, only terminated azo compound and unreacted coupling component are expected as by-products. Smaller amounts of miscouplings, disazo compounds, and polyaryls may also be found.

Table 7

COLOUR INDEX DESCRIPTIONS OF THE TRISAZO DYE AND PIGMENT SUBCLASSES

C.I. Number	Nature of Tetrazo Component	Number of Dyes[a] Included in This Study	Approximate 1978 U.S. Production (mt)[b]
Trisazo I (general formula $E \leftarrow D \rightarrow Z \leftarrow A$)			
30000-30030	p-Phenylenediamine	1	> 2.3
30035-30400	Benzidine and its congeners[c]	0	—
Trisazo II (general formula $E \leftarrow D \rightarrow M \rightarrow E'$)			
31500-32055	Phenylenediamine and its derivatives	1	> 9.1
	Benzidine and its congeners[c]	0	—
	Nature of Twice Coupled Component		
Trisazo III (general formula $A \rightarrow Z \leftarrow M \leftarrow A'$)			
33500-33999	m-Phenylenediamine and resorcinol		—
	Nature of End Component		
Trisazo IV (general formula $A \rightarrow M \rightarrow M' \rightarrow E$)			
34005-34025	2,5-Xylidine, cresidine, and m-diamines	1	> 2.3
34035	Phenol	0	—
34040-34060	Salicylic acid, and resorcinol	1	> 2.3
34080-34100	Naphthol sulfonic acid	2	9
34120-34180	J-acid, and Gamma acid	0	—
34200-34230	N-Phenyl-J-acid	2	> 4.5
34250-34255	N-Carbamoyl-J-acid	0	—
34260	N-m-Aminobenzoyl-J-acid	1	> 2.3
34270-34280	N-Acetyl-H-acid, and 2-methylindole	0	—
34285	2,4-Quinolinediol	0	—
34290-34300	Pyrazolones	0	—

Table 7 (Concluded)

COLOUR INDEX DESCRIPTIONS OF THE TRISAZO DYE AND PIGMENT SUBCLASSES

C.I. Number	Nature of Tetrazo Component	Number of Dyes[a] Included in This Study	Approximate 1973 U.S. Production (mt)[b]
Trisazo V (general formula $A \rightarrow \underset{\overset{\uparrow}{A''}}{Z} \leftarrow A'$ and $T \begin{smallmatrix} \nearrow E \\ \rightarrow E' \\ \searrow E'' \end{smallmatrix}$			
34900-34999	Various components	0	--
Tetrakis and Polyazo (combinations of above)			
3500-36999	Various components	4	216

---

[a] For which C.I. numbers were available.

[b] Many production values are reported as lower limits; thus the subclass production values are approximate.

[c] Azo dyes and pigments based on benzidine and its derivatives are not included in this study.

The Disazo I subclass is an extension of the monoazo class because a monoazo compound formed during the first coupling reaction is coupled with another diazo compound. This sequence is thus equivalent to two monazo coupling reactions in series. The by-products would be similar to those encountered during monoazo dye manufacture. The reaction conditions favor the disazo product; however, some monoazo compounds may remain.

The Disazo II subclass represents those dyes made from diaminoaryl compounds that are tetrazotized. The major by-product from this subclass is the terminated first-coupled product (or monoazo compound) that is incapable of coupling further. Also polyazo compounds could form from some diazo components.

The Disazo III subclass represents dyes made by successive diazotizations and couplings of arylamino compounds. Thus, initially, a coupling component with an amine or reducible nitro group is coupled to a disazo component to form a monoazo compound. The amine group is then diazotized and coupled to a second coupling component. This sequence of reactions would lead to a greater chance of nitrosamine formation from the terminated diazo component remaining from the first coupling reaction, because under the diazotization reaction conditions, the aryl chloride (or terminated by-product) may react with a primary amine, giving a secondary amine that could then form a secondary nitrosamine. The other types of by-products could be the terminated coupled product (monoazo compound) as well as the primary nitrosamines and polyaryls discussed previously.

The Disazo IV subclass is similar to Disazo I in the coupling reaction sequences and would also be similar in the type of by-products formed.

The Trisazo I subclass is made up of dyes similar to Disazo II dyes that have been coupled again on one of the end components of the disazo compound. The by-products from this category should be of the same type as the Disazo II subclass with the possible addition of some miscouplings between the excess coupling components added during the first two coupling reactions and the diazo component added during the final coupling reaction.

The Trisazo II and IV subclasses both require diazotization of a monoazo or disazo product before the next coupling reaction. In each subclass then the conditions exist (similar to Disazo III) for producing nitrosamines from terminated products that remain from the previous couplings.

Trisazo III subclass dyes are similar to the Disazo I subclass where a diazo component is coupled to the disazo compound. The by-products should be similar to the Disazo I subclass with the addition of miscouplings such as may occur between the final diazo component and any excess uncoupled or terminated disazo compound remaining in solution.

The Trisazo V subclass is unique in that a single coupling component capable of coupling in three positions is coupled with three diazo components (often dissimilar). The possible by-products would include incompletely coupled products (similar to Disazo I) and coupling components that had coupled twice with the same diazo component.

The Tetrakis and Polyazo classes include, in general, products from further coupling on trisazo compounds although some dyes are made by condensation of two disazo compounds with phosgene. The by-products from tetrakis and polyazo dye and pigment production are expected to be similar to the other azo dye classes.

The dye and pigment subclasses that would be most likely to have by-products other than terminated couplings or miscouplings (which are common to all subclasses) are the Disazo III, Trisazo II, IV, and all higher azo classes. This is due to the conditions during subsequent diazotization reactions and the possible formation of nitrosamines.

Several dyes and pigments require further steps to complete synthesis of the active color molecule. One such reaction is termed premetallization, when the dye molecule is complexed with metals such as chromium (III). Other dyes are completed by the condensation reactions of terminal hydroxyl groups with aryl sulfonyl chlorides to yield sulfonyl esters. These reactions and others are discussed below.

OTHER REACTIONS

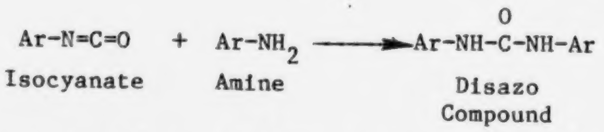
Phosgenation Reactions

Several of the disazo and higher azo dyes (many in the direct dye use class) are made by reacting two moles of monoazo compound containing a free amino group with phosgene (carbonyl chloride). This provides a way of preparing the higher azo dyes and pigments that are symmetrical.

The reaction takes place in two steps that produce an isocyanate as an intermediate.

$$\underset{\text{Monoazo}}{Ar\text{-}NH_2} + \underset{\text{Phosgene}}{COCl_2} \longrightarrow \underset{\text{Isocyanate}}{Ar\text{-}N{=}C{=}O} + 2HCl$$

The isocyanate reacts with any amine present to form a substituted urea.



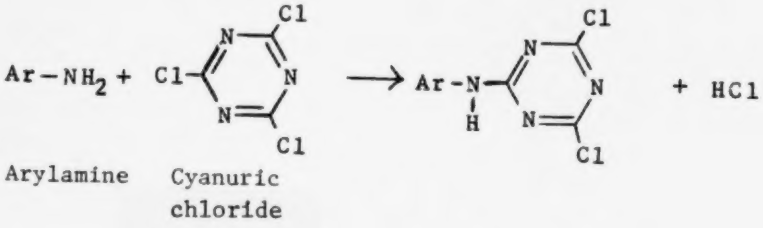
$$\underset{\text{Isocyanate}}{Ar\text{-}N{=}C{=}O} + \underset{\text{Amine}}{Ar\text{-}NH_2} \longrightarrow \underset{\text{Disazo Compound}}{Ar\text{-}NH\text{-}\overset{O}{C}\text{-}NH\text{-}Ar}$$

The reactions are conducted by bubbling phosgene-enriched air into the dye manufacturing vessel and monitoring the disappearance of amine. When water is present, as it is in an azo dye manufacturing operation, isocyanates yield substituted carbamic acids, which decarboxylate with extreme ease to yield the original amine. The amine can then react with isocyanate to give a symmetrically substituted urea. Consequently, it is very difficult to produce an unsymmetrical dye or pigment by phosgenation.

The phosgenation reaction is not likely to produce a significant amount of hazardous waste. It is assumed that phosgene was added with the amine always in excess and that the phosgenation reactions are complete (i.e., no free amines remain in the reaction liquor). The major organic reaction by-products are assumed to be the compounds produced by the reaction between phosgene and any unreacted coupling component (containing a free amine) remaining after previous coupling reactions. The resulting isocyanate can further react with any of the amines present to form substituted ureas.

Condensation Reactions of Cyanuric Chloride

Several monoazo dyes (many in the reactive dye class) are made by condensation reactions with cyanuric chloride. Cyanuric chloride will react with an aryl amino group in the partial dye molecule. Hydrogen chloride is a by-product of the reaction:



The chlorine atoms in cyanuric chloride are as highly reactive as in ordinary acid chlorides, but at 0°C no hydrolysis by water occurs in 12 hours.

Aniline and its ring-substituted derivatives react with cyanuric chloride to form primary, secondary, and tertiary condensation products. However, more complex amines undergo the third condensation with difficulty. If water-soluble amines, such as the sodium salts of arylamine sulfonic acids are used, the condensation may be affected in aqueous solution at 0°C. Higher temperatures (30-90°C) are necessary for the second and third replacements, or the third chlorine atom can be replaced by a hydroxyl or amino group.

These reactions were not studied in detail because the dyes involved are relatively minor and not likely to produce significant amounts of hazardous wastes. It was assumed that no excess cyanuric chloride was required and that chloride with excess aryl amine from previous from previous coupling reactions.

Esterification Reactions

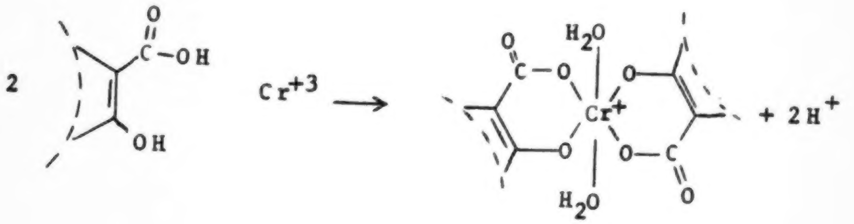
The synthesis of five azo dyes included in this study is completed through an esterification reaction instead of another coupling via an azo group. They are: Acid Yellow 65, Acid Yellow 40, Acid Yellow 38, Acid Orange 51, and Direct Yellow 12. p-Toluene sulfonyl chloride, benzene sulfonyl chloride, or ethyl chloride react with the hydroxyl group on the partial dye molecule. Hydrogen chloride is a by-product of the reaction:

$$ArSO_2Cl + Ar'OH \longrightarrow ArSO_2OAr' + HCl$$

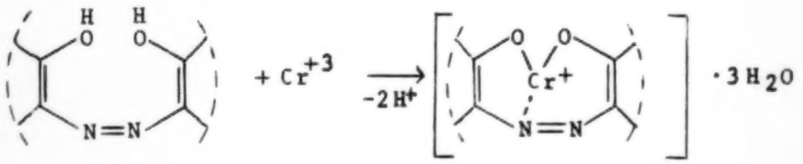
This reaction was not studied in detail because the dyes involved are relatively minor and not likely to produce significant amounts of hazardous wastes. It was assumed that no excess esterifying component was required and that the major reaction by-product was the condensation product of the esterifying component with excess coupling component, containing a hydroxyl group, from previous coupling steps.

Metal Complexes

Azo dyes can form complexes with metal ions. In forming the complex, unpaired electrons in parts of the molecule interact with coordination sites on the metal ion. These unpaired electron sites are called ligand groups in the following discussion. Many azo dyes have two or more ligand groups that are close together. These ligand groups can interact with several coordination sites on a single metal ion. For example, bifunctional azo dyes with salicylic acid as the coupling component have two ligand groups, a hydroxide group and a carboxylic acid group and can form 1:1 complexes (one metal ion to one dye molecule) with copper (II) or nickel (II) ions that have four coordination sites. These dyes also form 1:2 (one metal ion to two dye molecules) complexes with chromium (III) and cobalt (III) ions that have six coordination sites as illustrated below;



Trifunctional azo dyes with three ligand groups have amino or hydroxyl groups on both sides of the azo linkage. o,o'-Dihydroxyazo dyes are important members of this class. These dyes form 1:1 complexes with copper and nickel and 1:1 or 1:2 complexes with chromium or cobalt. The formation of a 1:1 complex with chromium is illustrated below.



The metal ion coordination sites that do not interact with the dye molecule can interact with water or ligand groups such as hydroxyl or amine groups on the fabric. The formation of the metal complex stabilizes the dye molecule, making it more resistant to degradation and sometimes aids in binding the dye to fabrics.

Several different procedures can be used to form the dye-metal complex (metallized dye):

- Precipitation and filtration of the organic dye followed by reaction of the diluted filter cake with metal salts. The metallized dye may be prepared for final processing by drying the entire reaction mixture rather than reprecipitation and filtering.
- Reaction of the metal with the organic dye molecule directly in the mother liquor before the product is precipitated and filtered.
- Some 1:2 complexes are prepared by reacting the 1:1 complex from either of the above two routes with unmetallized dye.

The commonly used metal salts in these reactions are the sulfates and formates although fluorides and acetates are also used. Based on the BIOS recipes, these salts may be formed in situ from the metal oxides and the appropriate acid. The metalization reactions are most often conducted in aqueous solutions although organics such as ethylene glycol and formamide (Abrahart, 1968) are sometimes present. Autoclaves are used for the metalization reactions because temperatures of up to 130°C may be used.

CHEMISTRY OF AZOIC COMPOUNDS

The azoic compounds, which include azoic diazo components, azoic coupling components, and azoic compositions, are dye intermediates that are used to produce colors directly on fibers.

Azoic diazo components are either diazonium salts or aromatic amines substituted by electronegative groups but free from water-solublizing groups that can be converted to diazonium salts in the dye bath and coupled to other aromatic molecules to produce the dye. The first amine used as an azoic diazo component was p-nitroaniline.

Azoic coupling components react with diazonium salts in the dye bath or on the fibers to form dyes. The majority of the azoic coupling components in use today are the substituted arylamides of 3-hydroxy-2-naphthoic acid. These coupling components are prepared generally by the condensation of 3-hydroxy-2-naphthoic acid (or its sodium salt) with the appropriate arylamine in boiling toluene with phosphorus trichloride as a condensing agent.

The azoic compositions are mixtures of diazonium salts and azoic coupling components. The mixture itself is placed in the dye bath, where the coupling reactions to produce a dye occur.

For the azoic coupling and diazo components included in this study, the chemistry involved in the preparation of the components does not include reactions such as diazotization and coupling. They are made using the same kind of chemical reactions that are used to make the other intermediates (which are used to manufacture azo dyes and pigments). These chemical reactions and the residuals they produce were not included in this discussion because they were too varied to discuss in any significant manner. The azoic compounds are considered to be purchased as is or transferred from other manufacturing facilities at the dye and pigment manufacturing site.

SECTION 4

DYE INTERMEDIATES

A list of the intermediates used in manufacturing azo dyes and pigments in the United States was compiled from information in the Colour Index (The Society of Dyers and Colourists, 1980). Intermediates used to manufacture dyes and pigments whose ingredients were not published in the Colour Index could not be included in the list. Table 8 lists the organic intermediates for which some physical property data were found in OHMTADS* and Hansch (1978). (These physical properties are listed because they are used later in this report to discuss the emissions of intermediates during the dye manufacturing process.)

All the intermediates listed in Table 8, except the liquids, aniline, and some substituted anilines, have melting points above ambient temperature, which means that they will be solids when received at the dye manufacturing site. Nearly all the intermediates are estimated to have low vapor pressures (<1 mm Hg at ambient temperatures). Some are reported to have substantial vapor pressures at high temperatures, but when the vapor pressure versus temperature data is extrapolated to ambient temperatures, the result is an insignificant vapor pressure. Thus, even though 2-naphthol has a vapor pressure of 100 mm Hg at 206°C, its vapor pressure will be far less than 1 mm Hg at 20 °C. The low vapor pressures are mirrored in the high boiling points for most of the compounds.

The low vapor pressures mean that vapor losses from manufacturing steps at ambient temperature will be minor. Even at 100°C, most of the compounds have vapor pressures far less than water. Any of these low-vapor-pressure unreacted intermediates that accompany precipitated and filtered dye or pigment will volatilize much more slowly than water during the final product drying step. They will therefore remain on the dye or pigment solids after all of the water has evaporated.

Table 8 also gives the log of the octanol-water partition coefficients. In general, these values are low, indicating that the compounds are not likely to concentrate in lipid materials. Another environmentally important parameter is K_{oc}, which indicates the tendency of organic chemicals to adsorb

---

*OHMTADS is an online data system that is a component of the Chemical Information System (CIS) operated by the National Institute of Health and the U.S. Environmental Protection Agency.

Table 8

ORGANIC INTERMEDIATES AND OTHER CHEMICALS USED IN AZO DYE AND PIGMENT MANUFACTURE FOR WHICH PHYSICAL PROPERTY DATA WERE FOUND[a]

Intermediate	Vapor Pressure (mm Hg, °C)		Solubility in Water (ppm at 25°C)	Log Octanol-Water Partition Coefficient	MP (°C)	BP (°C)
Substituted Naphthalene Compounds						
1-Aminonaphthalene	1	104	Soluble	2.25	50	301
1-Hydroxynaphthalene	<0.1	20	Insoluble	2.6	95	150
2-Hydroxynaphthalene	100	206	1,000	2.8	122	288
7-Amino-1,3-naphthalene disulfonic acid	--	--	Soluble	--	273	--
1-Amino 8-hydroxy-3,6-naphthalene disulfonic acid	--	--	Slightly	--	--	--
2-Hydroxy-3,6-naphthalene disulfonic acid	--	--	Very	--	--	--
2-Hydroxy-6,8-naphthalene disulfonic acid	--	--	Very	--	--	--
4,5-Dihydroxy-2,7-naphthalene disulfonic acid	--	--	Soluble	--	220	--
2-Amino-1-naphthalene sulfonic acid	--	--	Slightly	--	--	--
4-Amino-1-naphthalene sulfonic acid	--	--	Insoluble	--	[b]	--
1-Hydroxy-4-naphthalene sulfonic acid	--	--	Very	-0.44	170[b]	--
1-Hydroxy-5-naphthalene sulfonic acid	--	--	Soluble	-0.17	120	--
1-Hydroxy-8-naphthalene sulfonic acid	--	--	Very	--	107	--
2-Hydroxy-6-naphthalene sulfonic acid	--	--	Very	--	125	--
3-Hydroxy-2-naphthalene carboxylic acid	--	--	Insoluble	--	220	--
Substituted Aniline Compounds						
Aniline	<1	25	35,000	0.92	-6	184
p-Nitroaniline	101	106	800	1.39	148	322
2,4-Diaminotoluene	1	100	Very	--	99	292
m-Phenylenediamine	1	100	3 x 10^5	--	63	287
Cresidine (3-amino-4-methoxytoluene)	--	--	Slightly	--	93	235
4,4'-Thiodianiline	--	--	Slightly	--	108	--
2,4'-Thiodianiline	--	--	Slightly	--	62	--

Table 8 (Continued)

Intermediate	Vapor Pressure (mm Hg,	°C)	Solubility in Water (ppm at 25°C)	Log Octanol-Water Partition Coefficient	MP (°C)	BP (°C)
o-Phenylazoaniline	--	--	Slightly	--	128	>360
2,4-Dichloroaniline	> 0.1	20	Slightly	2.6	63	245
m-Aminobenzoic acid	--	--	Slightly	0.28	174	--
p-Aminobenzoic acid	--	--	Slightly	0.46	187	--
o-Anisidine (2-methoxyaniline)	1	61	Insoluble	0.95	5	220
2-Nitro-p-anisidine	--	--	Soluble	--	123	--
4-Nitro-o-anisidine	--	--	--	--	140	--
5-Nitro-o-anisidine	--	--	Slightly	--	118	--
2,4-Diaminotoluene	1	106	Soluble	--	94	280
2,6-Diaminotoluene	1	106	Soluble	--	105	--
o-Toluidine (2-aminotoluene)	1	44	15,000	1.3	-16	200
m-Toluidine (3-aminotoluene)	1	41	Slightly	1.4	-30	203
4-Chloro-o-toluidine	--	--	--	--	29	241
2-Nitro-p-toluidine	--	--	Slightly	--	117	--
5-Nitro-o-toluidine	--	--	Slightly	--	107	--
o-Chloroaniline	1	46	Insoluble	1.9	-14	209
p-Chloroaniline	1	59	Slightly	1.7	71	231
2-Chloro-4-nitroaniline	--	--	Slightly	--	104	--
4-Chloro-2-nitroaniline	--	--	--	--	115	--
2,5-Dichloroaniline	< 0.1	20	Slightly	2.5	20	251
2,6-Dichloro-4-nitroaniline	<<.01	20	Insoluble	--	191	--
N,N-Diethylaniline	1	50	14,000	3.3	-38	216
N,N-Dimethylaniline	1	29	Insoluble	2.3	2.4	193
2,4-Dinitroaniline	--	--	Insoluble	--	170	--
2,4,5-Trichloroaniline	--	--	--	3.27	96	270
o-Nitroaniline	1	104	4,700	1.8	71	284
m-Nitroaniline	--	--	1,100	1.37	114	306

Table 8 (Continued)

Intermediate	Vapor Pressure (mmHg, °C)		Solubility in Water (ppm at 25°C)	Log Octanol-Water Partition Coefficient	MP (°C)	BP (°C)
p-Aminophenol	<0.1	20	5,600	0.04	186	284[b]
2-Amino-5-nitrophenol	--	--	--	--	201	--
2-Amino benzene sulfonic acid (orthanilic acid)	--	--	Slightly	--	325[b]	--
4-Amino benzene sulfonic acid (sulfanilic acid)	--	--	10,000	--	288[b]	-- --
4-Amino-6-nitro-4-phenol sulfonic acid	--	--	Slightly	--	--	--
2-Amino-4-phenol sulfonic acid	--	--	Slightly	--	155	--
5-Amino-2,4-xylene sulfonic acid	--	--	Slightly	--	290[b]	--
4-Amino-3-toluene sulfonic acid	--	--	Slightly	--	132[b]	--
2-Amino benzene carboxylic acid (anthranilic acid)	--	--	Slightly	1.2	145	--
4-Amino benzamide	--	--	Slightly	0.02	183	--
Diphenvl amine	1	108	Insoluble	3.5	54	310
2,4-Xylidine	<0.1	20	Slightly	--	16	215
2,5-Xylidine	.14	20	Slightly	--	15	214
N-(3-Aminophenyl) acetamide	--	--	Very	--	87	--
N-Ethyl-N-phenyl benzylamine	--	--	Insoluble	--	--	285
2-Amino-4,6-dinitro-phenol	--	--	650	0.93	169	--

Table 8 (Concluded)

Intermediate	Vapor Pressure (mmHg, °C)		Solubility in Water (ppm at 25°C)	Log Octanol-Water Partition Coefficient[a]	MP (°C)	BP (°C)
Other Intermediates						
p-Cyclohexylphenol	--	--	--	4.2	120	--
p-Nitrobenzoyl chloride	--	--	Decomposes	--	75	202
Cyanuric chloride	2	70	Insoluble	--	150	194
2-(N-Methylanilino) ethanol	--	--	Slightly	--	--	150
p-Aminoacetanilide	--	--	--	0.08	162	--
Acetoacetanilide	0.01	20	Slightly	--	85	b
p-Cresol	1	50	24	1.95	36	201
o-Cresol	1	38	31	1.95	31	190
3-Methyl-1-phenyl-5-pyrazolone	--	--	Slightly	--	127	287
3-Methyl-1-(p-sulfophenyl)-5-pyrazolone	--	--	Slightly	--	290[b]	--
Benzenesulfonyl chloride	1	66	Insoluble	--	14	251[b]
1-Methyl-2-phenyl-1-H-indole	--	--	--	--	98	200
2-Hydroxybenzoic acid	1	114	2,000	2.3	157	b
Diazoaminobenzene	--	--	Insoluble	--	98	b
Resorcinol	20	168	100,000	0.78	111	281
Phenol	60	86	67,000	1.5	43	182
Solvents and Reagents						
Ethanol	40	19	Miscible	-0.3	-115	78
Phosgene	1180	20	Slightly	--	-118	8
Formaldehyde	10	-88	555,000	--	-92	-19
Pyridine	20	25	Miscible	0.62	-42	115
Formamide	29	129	Miscible	-1.51	2.5	210

---

[a] Source: OHMTADS, Kirk-Othmer (1978), Hansch (1978) for partition coefficients.

[b] Decomposes.

to the organic material in soils and sediments (Smith et al., 1977, 1978). It has been shown that for organic chemicals the overall potential for adsorption to soil and sediment is the product of K_{oc} and the fraction of the soil or sediment that is organic (Kenaga and Goring, 1978). K_{oc} values have been measured for many pesticides and common organic chemicals. This work has shown that K_{oc} and the octanol-water partition coefficient (K_{ow}) values are related. Mabey et al. (1981) present the relationship $\log K_{oc} = \log K_{ow} - 0.21$, which was derived statistically, to predict K_{oc} values from K_{ow}. Based on this relationship it can be predicted that few of the chemicals in Table 8 with known K_{ow} values would have K_{oc} values much greater than 100. Our experience (Smith et al., 1977, 1978) indicates that sorption to the organic material in soils and sediments is not significant for compounds with such low values for K_{oc}.

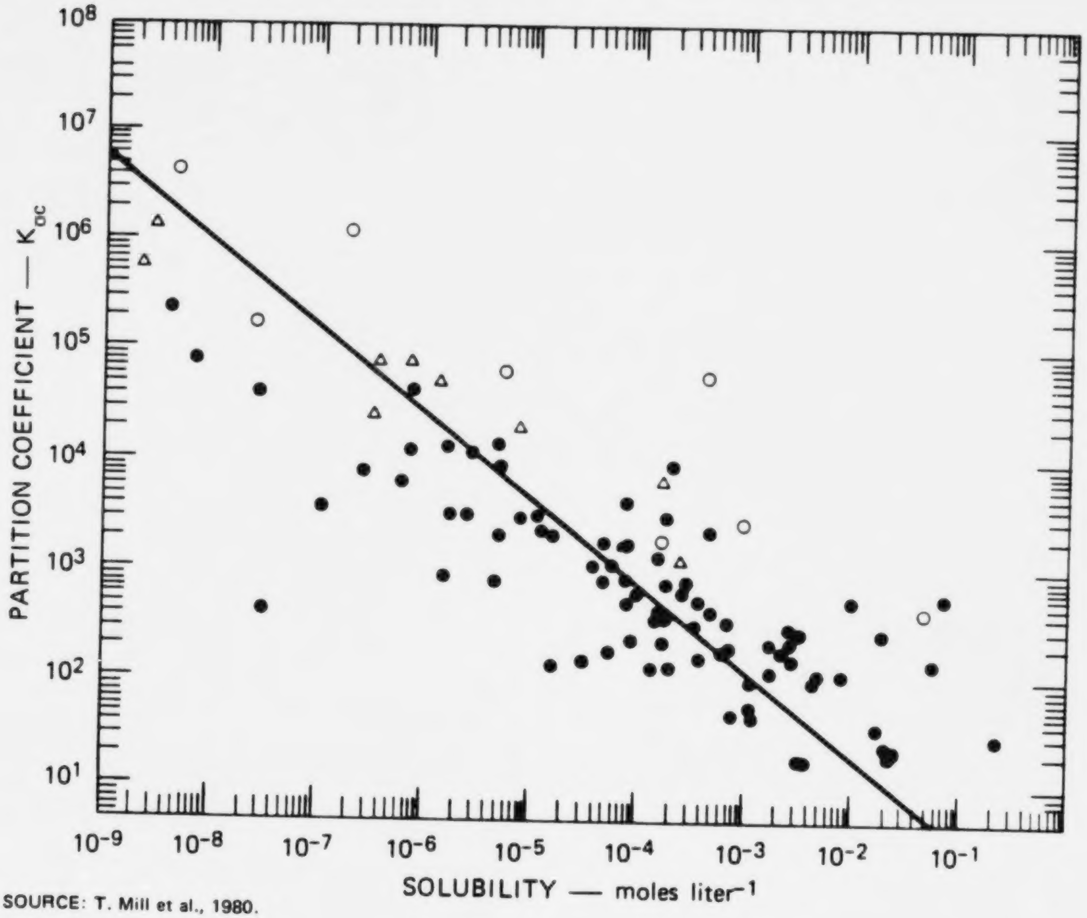
The solubility data in Table 8 are hard to interpret because it was not possible, given the scope of this study, to review the individual data sources. It is assumed, however, that "slightly" indicates solubilities of about 100 ppm and that "soluble" indicates solubilities of about 1000 ppm. Of the intermediates listed, aniline, resorcinol, 2,4-diamino toluene, m-phenylenediamine, and some of the substituted naphthalene sulfonic acids have substantial solubilities.

Included in Table 8 are solvents and other chemicals that are not considered intermediates but are added during the synthesis of several dyes. These compounds have significant vapor pressures at 20°C, low melting points, and appreciable solubility in water. With the exception of phosgene, which is a gas, they are all liquids.

The high vapor pressures of these compounds will lead to vapor losses in all phases of the dye manufacturing operation in which they are employed. Phosgene is so volatile that it is not expected to remain in the mother liquor at all. The others will persist to some degree in the mother liquor. When the dye or pigment product is dried, any that is carried in entrained mother liquor will volatilize and be carried into the air pollution control system.

Several workers have shown that solubility and K_{oc} are inversely related. Figure 1, which is from a review of solubility relationships (Mill et al., 1980), shows that compounds that are soluble in water, such as the liquid solvents and reagents, are likely to have low K_{oc} values. Even formaldehyde, which is the least soluble, has a molar solubility of greater than 1 and is predicted to have a K_{oc} value of less than 1. Thus, these materials will not sorb strongly to soils and sediments when released.

Table 9 lists the more highly substituted organic intermediates used in the United States to manufacture azo dyes and pigments. The names in parenthesis are common names that are often used. No physical property data were found for these compounds in the sources searched. They are assumed to have properties similar to the majority of those in Table 8, i.e., low vapor pressure, solid at ambient temperature, and not strongly adsorbed to organic material or soils and sediments. Because many of these compounds have multiple sulfonic acid and/or hydroxyl functional groups, they may be more soluble than the intermediates listed in Table 8.



SOURCE: T. Mill et al., 1980.

SA-4396-85B

FIGURE 1 SOIL OR SEDIMENT PARTITION COEFFICIENT OF CHEMICALS VERSUS SOLUBILITY IN WATER

Table 9

ORGANIC INTERMEDIATES FOR WHICH NO PHYSICAL PROPERTY DATA WERE FOUND

Substituted Naphthalene Disulfonic Acid Compounds

2-Amino-1,5-naphthalene disulfonic acid	
3-Amino-1,5-naphthalene disulfonic acid	
4-Amino-5-hydroxy-1,3-naphthalene disulfonic acid	(Chicago acid)
4,8-Diamino-2,6-naphthalene disulfonic acid	
1-Hydroxy-3,6-naphthalene disulfonic acid	
1-Hydroxy-3,8-naphthalene disulfonic acid	
N-Acetyl-1-amino-8-hydroxy-3,6-naphthalene disulfonic acid	(N-Acetyl H acid)
o-Phenylsulfonyl-1-amino-8-hydroxy-3,6-naphthalene disulfonic acid	(o-Phenylsulfonyl H acid)
o-Tolylsulfonyl-1-amino-8-hydroxy-3,6 naphthalene disulfonic acid	(o-Tolylsulfonyl H acid)
o-Phenylsulfonyl-2-amino-8-hydroxy-3,6-naphthalene disulfonic acid	(o-Phenylsulfonyl 2 R acid)

Substituted Naphthalene Sulfonic Acid Compounds

1-Amino-4-naphthalene sulfonic acid	(Naphthionic acid)
1-Amino-6-naphthalene sulfonic acid	(1,6-Cleve's acid)
1-Amino-7-naphthalene sulfonic acid	(1,7-Cleve's acid)

Table 9 (Continued)

1-Amino-2-hydroxy-4-naphthalene sulfonic acid	
1-Amino-8-hydroxy-4-naphthalene sulfonic acid	(S acid)
1-Amino-2-hydroxy-6-nitro-4-naphthalene sulfonic acid	
2-Amino-6-naphthalene sulfonic acid	(Bronners acid)
5-Amino-1-naphthalene sulfonic acid	
5-Amino-6-ethoxy-2-naphthalene sulfonic acid	
6-Amino-4-hydroxy-2-naphthalene sulfonic acid	(Gamma acid)
7-Amino-4-hydroxy-2-naphthalene sulfonic acid	(J acid)
4,6-Dihydroxy-2-naphthalene sulfonic acid	
6,6'Iminobis-1-hydroxy-3-naphthalene sulfonic acid	
N-Acetyl-2-amino-5-hydroxy-7-naphthalene sulfonic acid	(N-Acetyl-J acid)
N-Acetyl-7-amino-1-hydroxy-3-naphthalene sulfonic acid	(N-Acetyl Gamma acid)
N-Phenyl-1-amino-8-naphthalene sulfonic acid	(N-Phenyl Peri acid)
N-Phenyl-2-amino-8-hydroxy-6-naphthalene sulfonic acid	(N-Phenyl Gamma acid)
N-Phenyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	(N-Phenyl J acid)
N-Benzoyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	(N-Benzoyl J acid)
N-m-Aminobenzoyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	(N-m-Aminobenzoyl J acid)
N-p-Aminobenzoyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	(N-p-Aminobenzoyl J acid)
N-p-Tolyl-1-amino-8-naphthalene sulfonic acid	(N-p-Tolyl Peri acid)

Substituted Naphthalene Compounds

3-Hydroxy-2-naphthalene carboxylic acid

3-Hydroxy-2-naphthalene-o-anisidide

Table 9 (Continued)

3-Hydroxy-2-naphthalene-o-toluidide
4'-Chloro-3-hydroxy-2-naphthalene-o-toluidide
3-Hydroxy-2-naphthanilide
3-Hydroxy-2',5'-dimethoxy-2-naphthanilide
3-Hydroxy-3' -nitro-2-naphthanilide
4'-Acetamido-3-hydroxy-2-naphthanilide
4'-Chloro-3-hydroxy-2',5'-dimethoxy-2-naphthanilide
5'-Chloro-3-hydroxy-2',4'-dimethoxy-2-naphthanilide
N-Ethyl-2-aminonaphthalene
N-(7-Hydroxy-1-naphthyl)acetamide

Substituted Pyrazolone Compounds

3-Methyl-1-p-tolyl-5-pyrazolone
3-Carbethoxy-1-phenyl-5-pyrazolone
3-Carboxy-1-(m-nitrophenyl)-5-pyrazolone
3-Carboxy-1-(p-sulfophenyl)-5-pyrazolone
1-(4-Chloro-2-sulfophenyl)-3-methyl-5-pyrazolone
1-(2-Chloro-5-sulfophenyl)-3-methyl-5-pyrazolone
1-(2,5-Dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone
3-Methyl-1-(2,4-dichloro-4-sulfophenyl)-5-pyrazolone
3-Methyl-1-(m-sulfophenyl)-5-pyrazolone
3-Methyl-1-(4-sulfo-o-tolyl)-5-pyrazolone
1-(6-Chloro-o-tolyl)-3-methyl-5-pyrazolone

Substituted Benzene Sulfonic Acid Compounds

2-Amino-5-nitrobenzene sulfonic acid
2-Amino-1-hydroxy-4-benzene sulfonic acid
2-Amino-5-chloro-4-ethyl benzene sulfonic acid
2-Amino-5-methoxybenzene sulfonic acid

Table 9 (continued)

2-Amino-4-(3-chloro-1-oxido-1,2,4-benzotriazene-7-carboxamide) benzene sulfonic acid

2-Amino-5-(4-amino-3-sulfo-1-anthraquinonylamino) benzene sulfonic acid

2,4-Diaminobenzene sulfonic acid

3-Amino-4-methoxybenzene sulfonic acid

5-Amino-2-(p-aminoaniline) benzene sulfonic acid

6-Amino-4-chloro-1-hydroxy-2-benzene sulfonic acid

6-Amino-4-nitro-1-hydroxy-2-benzene sulfonic acid

6-Amino-3,4'-azodibenzene sulfonic acid

(2-(p-Aminoanilino)-5-nitrobenzene sulfonic acid

5-Acetamide-2-aminobenzene sulfonic acid

p-(p-Aminophenylazo)-benzene sulfonic acid

5,5'-Ureylenebis(2-aminobenzene sulfonic acid)

2-Amino-5-chloro-p-toluene sulfonic acid

4-Amino-5-methoxy-o-toluene sulfonic acid

6-amino-4-chloro-m-toluene sulfonic acid

6-Amino-m-toluene sulfonic acid

p-Amino-α-toluene sulfonic acid

4,6-Diamino-m-toluene sulfonic acid

2-Amino-3,5-xylene sulfonic acid

Substituted Acetoacetic Amides

o-Acetoacetotoluidide

p-Acetoacetotoluidide

o-Acetoacetanisidine

4'-Chloro-o-acetoacetotoluidide

4,4'-Bi-o-Acetoacetotoludine

2,4-Acetoacetoxylidide

p-Acetoacetophenetidide

o-Chloroacetoacetanilide

4'-Chloro-2',5'-dimethoxyacetoacetanilide

2,4-Acetoacetoxylidine

4'-Chloro-2',5'-dimethoxyacetoacetanilide

Table 9 (Continued)

Other Compounds

m-Aminoformanilide
5-Amino-1,4-dimethyl-1H-1,2,4-triazole
2-Amino-3-methylthiazole
2-Amino-6-methoxy-3-methylbenzothiazole
2-Amino-N-methyl-1-phenol-4-sulfonamide
2-Amino-1-phenol-4-sulfonamide
2-(N-Ethylanilino)ethanol
2-(4-Amino-3,6-dimethoxyphenylsulfonyl)ethanol sulfate ester
2-(4-Amino-3-methoxyphenylsulfonyl)ethanol sulfate ester
2-(p-Aminophenylsulfonyl)ethanol sulfate ester
2,2'-(m-Tolylimino)diethanol
2,2'-(m-Chlorophenylimino)diethanol
3-Hydroxy-2-naphtho-o-phenetidide

2,5-Dimethoxyaniline
N-Methyl-N-(2,3-dimethoxypropyl)aniline
m-Diethylaminoacetanilide
3-Amino-p-anisanilide
Methanilic acid
2-Amino-N-ethylbenzenesulfonanilide
4-Amino-2,5-dimethoxybenzenesulfonanilide
5-Amino-o-toluenesulfonanilide
3-(2-Chloroanilino)propionitrile
3-(N-2-Cyanoethylanilino)propionic acid methyl ester
3-(N-Ethylanilino)propionitrile
3-(N-Ethyl-m-toluidino)propionitrile
3-(N-2-Hydroxyethylanilino)propionitrile, acetate ester
3-(N-Methylanilino)propionitrile

Anilinomethanesulfonic acid
o-Toluidinomethanesulfonic acid
dihydrothio-p-toluidinesulfonic acid
Sodium dihydrothio-p-toluidinesulfonate

Table 9 (Continued)

Ethyl acetoacetate
p-Phenylazoaniline
2,5-Xylidine
2,4-Dichloroaniline
o-Toluidide
m-Aminoformanilide
p-Aminooxanilic acid
3-Methyl-2-hydroxybenzoic acid (2,3-Cresotic acid)
4-Sulfoanthranilic acid
2,4-Quinolinediol
2-Amino-N-methylpyridinium salt
1-Naphthol-8-sulfonamide
N,N-Diethyl-4-methoxymetanilamide

2-5-Dichlorosulfanilic acid
3-Amino-4-chlorobenzamide
5-(p-Aminophenylazo)-salicylic acid
N-(3-Amino-4-sulfophenyl)glycine
Xylylazoxylidine
p-Toluenesulfonyl chloride

4,4'-Benzylidenedi-2,5-xylidine
4,4'-(o-Chlorobenzylidene)di-2,5-xylidine
4,4'-Cyclohexylidenedi-o-anisidine
4,4'-Diamino-2,2'-stilbene disulfonic acid
6,6'-Thiodemethanilic acid
3,3'-Diaminobenzanilide
4-o-Tolyazo-o-toluidine
4-Nitro-m-phenylenediamine,Diazotized
Toluene-2,4-diamine hydrochloride
4-Methoxy-m-phenylenediamine

Table 9 (Concluded)

m-Phenylenediamine
p-Nonylphenol
4,4'-Cyclohexylidenedi-o-toluidine

2-Amino-5-nitrobenzonitrile
[2-(N-Ethylanilino)ethyl]trimethylammonium salt
2-Amino-4-(2,5-dichlorophenylcarbamoyl)benzoic acid methyl ester
(p-Aminobenzoylmethyl)trimethylammonium chloride
2-Amino-5-nitroisophthalonitrile
6-Chlorometanilic acid
2-Bromo-4,6-dinitroaniline
4-Chloro-α,α,α-trifluoro-o-toluidine
α,α,α-trifluoro-o-toluidine
m-Diethanolamino-p-methoxyacetanilide
3-(N-2-Hydroxyethylanilino)-propionitrile, acetate ester

SECTION 5

SOURCES OF WASTE DISCHARGES DURING AZO DYE AND PIGMENT MANUFACTURE

The wide range of azo dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, though, the most significant material losses will be intermediates that do not react and by-products, such as incomplete dye or pigment molecules. The intermediates and by-products from dye manufacture are present either in the product or in the solid waste streams regulated under RCRA--wastewater, solid residues, or the vapor and dust emissions. The material in the wastewater may be discharged in the plant effluent (although some will be destroyed by treatment as described below), and some will be discharged on wastewater treatment solids.

Published information and industry contacts concerning the presence of organic materials in the wastewaters of several unit operations of dye production (e.g., Steadman et al., 1977; Lapp et al., 1979; Abrahart, 1968; Boeniger, 1980) were used to develop materials release estimates for intermediates, by-products, and dyes and pigments in the azo dye and pigment manufacturing processes.

This section first gives a general overview of azo dye and pigment production processes and then describes the bases used for developing estimates of the amounts of material lost (expressed as a percentage of the finished and standardized dye or pigment). The losses from both dye and pigment manufacture are discussed below according to the stages of production in which they would occur (i.e., raw material receiving, synthesis, drying, grinding, standardization, blending, and packaging).

The solid residues are assumed to be placed in a landfill, either on the manufacturing property or at a commercial facility. The process wastewaters are processed through a wastewater treatment system that may include physical, chemical and/or biological treatment of all or just some of the effluent. In some cases, the wastewater treatment system may discharge partially treated wastewater to municipal treatment systems. Concentrated aqueous waste streams may also be concentrated further and landfilled. The actual environmental releases that occur after wastewater treatment are discussed at the end of the section.

OVERVIEW OF AZO DYE AND PIGMENT PRODUCTION PROCESSES

Figure 2 illustrates the dye and pigment manufacturing process and shows where the losses of materials occur. The dye manufacturing equipment required to produce azo dyes and pigments consists of well-stirred tanks, plate and frame filter presses, dryers, grinders, and blenders.

A dye or pigment is usually prepared in batches, and the plants typically contain several reactor trains. Each train includes at least one diazotization reactor, one coupling reactor, and one filter press. Complex dyes and pigments may require use of several reactor trains. Production of colors is usually rotated by set schedules from light- to dark-colored dyes or a train may be used exclusively for production of one color or one dye.

After diazotization, coupling, and any other chemical reactions are completed as described in Section 3, the water-soluble acid, direct, and reactive dye materials are precipitated (salted out) by the addition of salt to give a final brine concentration of up to 20% weight by volume (BIOS, 1945; Abrahart, 1968). The resulting slurry is filtered using a filter press, and air is blown through the presscake to remove as much mother liquor as possible (Kent, 1974). The cake is removed from the press and dried in an atmospheric tunnel dryer or a vacuum tray dryer. The dye is then ground in a swing hammer mill and thoroughly mixed in a blender.

Often sodium chloride or Glauber's salt (sodium sulfate) is added to the blender to reduce the water-soluble dye concentration to a standard strength (so-called standardization). The amount of salt added to a dye depends on the dye and the producer and may even vary among dye batches at a single facility. Various estimates of the percentage of inert salt in the final, marketed, water-soluble dye product included in this study are as follows:

<75%	(Gerber, 1980)[*]
50%-92%	(Steadman et al., 1977)
50%	(Shreeve and Brink, 1977)
45%-65%	(DETO, 1980)

An inert salt level of 50% has been assumed in the discussion that follows. (An estimate of the salt content of the standardized final product is necessary in discussing actual waste amounts produced by dye manufacturers because the majority of available production data are for the standardized dye.)

---

[*] Personal communication, S. Gerber, American Cyanamid Company; Sept. 8, 1980.

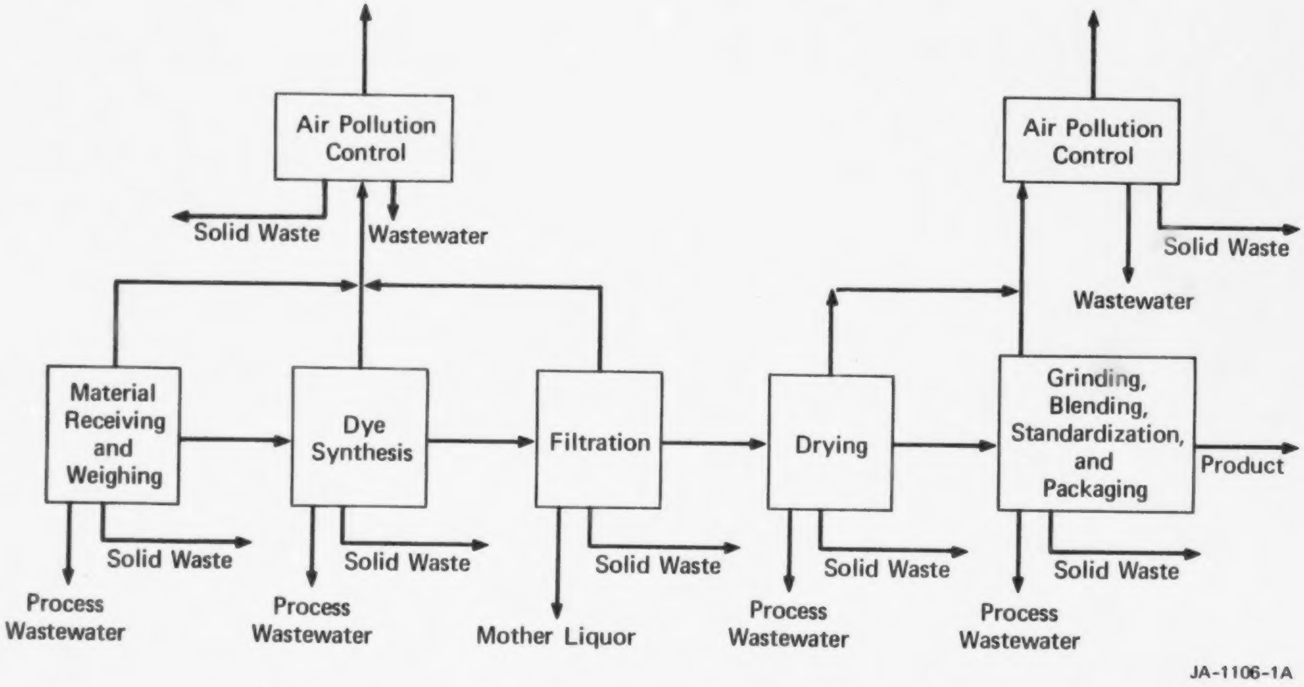

Air Pollution Control
Solid Waste
Wastewater
Air Pollution Control
Solid Waste
Wastewater
Material Receiving and Weighing
Dye Synthesis
Filtration
Drying
Grinding, Blending, Standardization, and Packaging
Product
Solid Waste
Process Wastewater
Solid Waste
Process Wastewater
Solid Waste
Mother Liquor
Solid Waste
Process Wastewater
Solid Waste
Process Wastewater
JA-1106-1A

FIGURE 2 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSIONS IN DYE AND PIGMENT MANUFACTURE

Pigments and disperse and solvent dyes are insoluble and do not require salting out. After filtration from the mother liquor, 45% of all pigments are dried, ground, and sold without dilution (Lapp et al., 1979). Another 40% are flushed (dispersed into an oil phase). On the basis of information from Steadman (1977), we have assumed that flushing adds 65% inert ingredients. The remaining 15% of all pigments are sold as wet filter press cake without processing. This means that, on the average, 27.5% of the final product sold is inert ingredients: (45% x 0% inert salt) + (40% x 65% oil) + (15% x 10% water in press cake) = 27.5% inert ingredients.

The disperse dyes may be sold as 100% product or flushed with a dispersing agent (sulfonated oil) and a surfactant. This may add 10-25% inerts.

The solvent dyes are generally sold as 100% product (i.e., dried, ground, and sold without dilution).

It was assumed that the water-insoluble dyes (solvent and disperse) and pigments contain 25% inert ingredients. The release estimates for each process step are developed separately for the water-soluble dyes and the water- insoluble dyes and pigments. An average diluent value of 25% was chosen to encompass the water insoluble dyes and pigments and 50% for the water-soluble dyes.

RAW MATERIAL RECEIVING AND HANDLING

Dye intermediates are received either from other chemical manufacturing sites or from manufacturing operations at the dye manufacturing site. The physical properties of the chemical intermediates for which data were found (see Table 8) indicate that they are almost all solids at ambient temperatures. The intermediates for which no data were found were assumed to be solids also because they are chemically similar to the intermediates with known properties and often of higher molecular weight. Therefore, material from other manufacturing sites is likely to arrive in fiber drums or paper bags. Material from the same site may arrive the same way or in some container such as a tote box designed for transfer and temporary storage of solids. The intermediates are weighed and transferred into the appropriate vessels in the dye reactor train.

Solid Residues

Most solid residues from material receiving will be shipping containers contaminated by chemicals that stick to the walls or fill cracks and crevices. It has been estimated that 0.1% of such solids remains in the shipping container. Very few data are available to indicate the disposition of this material. One industry contact* stated that his company which manufactures azo dyes and pigments, sends about one truckload of fiber drums and paper waste to a dump every day. Thus any chemicals in the drums or on the paper would be transferred to the dump site. Manufacturing operations that receive material in temporary storage and transportation containers from their own chemical manfuacturing operation may wash the containers and return them to duty so that any chemicals remaining in the containers would then go into the process wastewater treatment system.

To indicate the order of magnitude of the potential solid residue disposal required by azo dye and pigment manfuacturing, it has been assumed that all intermediates arrive in fiber drums or bags, which are later disposed of in a landfill.

We have estimated that 0.1% of the material in a bag or drum is retained in cracks or as a coating on wall surfaces when the container is emptied. This would represent only 0.05 lb of material in a 50-lb bag and less than 0.25 lb in a 30-gallon drum.

Because the water-soluble dyes have been assumed to be 50% inert salts, a 0.1% loss of the delivered intermediates is equivalent to a total intermediate loss of 0.05% on a final marketed product basis. Thus the manufacture of 100 pounds of a standardized monoazo dye would result in a total of 0.05 pound of intermediates in discarded drums and bags. However, because monoazo dyes require two intermediates, there would be only 0.025 pound of each intermediate if we assume that all the intermediates all have approximately the same molecular weight. (Because of the assumptions used to obtain the 0.05% estimate for material loss from material handling, it was not considered reasonable to correct for molecular weight differences when estimating the residue production for each dye). Disazo dyes require three intermediates so that the loss of each intermediate would be only 0.017 pound. In general, the solid residue associated with each intermediate is determined by dividing 0.05% by the number of intermediates used to build the dye molecule. For dyes that are premetallized, the metal is considered as an additional intermediate.

The assumption of similar molecular weights for all intermediates is not unreasonable even when metals are included in the dye. A common source of chrome for dyes is chromium formate, which has a molecular weight of 187, or chrome oxide, which has a molecular weight of 152, compared to a molecular weight of 93 for aniline or 144 for β-naphthol, which are both common organic intermediates in azo dye production. The chromium in the dye might have an equivalent molecular weight of 87.5 or 123 because of the chlorides necessary to make a neutral salt when the dye precipitates. Metals may actually be lost in their oxide form because the metal formate is often made in situ from the oxide.

---

*Personal communication M. B. Bochner, Atlantic Chemical Corporation, Sept. 10, 1980.

The same general procedure was followed for pigments and disperse and solvent dyes, which are assumed to be 75% active ingredients. For these dyes the total amount of intermediate in the solid residue stream would be 0.075% of the final marketed product. This amount was divided by the number of intermediates to determine the loss for each intermediate.

In this procedure for calculating intermediate solid residue losses, several special cases need to be treated. Some dyes use phosgene to couple two aromatic amines together. Phosgene is not counted as an intermediate because its total weight contribution to the final product is very small (equivalent to urea). Phosgene is generated on-site from gaseous ingredients (such as carbon monoxide and chlorine), and its use would not result in a solid residue. Cyanuric chloride, which is used for various dyes, is counted as an intermediate but is not included in the solid residue stream from materials handling. It is made on-site from gaseous and volatile liquid components (such as HCN, chloroform and chlorine).

Process Wastewater

The material from spills during transfer operations and residual material in temporary storage and transfer containers may be washed away. The amount of water required and the frequency of cleaning is difficult to quantify, and no quantitative estimates have been made.

Vapor and Dust Losses

Vapor losses during chemical intermediate transferring and weighing operations are expected to be small because most of the chemicals are estimated to have low vapor pressures and to be solids at room temperature. The loss of solid material from dusts may occur during handling. The vapors and dusts at the weighing and tranfer operations at some facilities will be vented to a scrubber unit (DETO, 1980; Keinath, 1976). In this study, the vapor and dust losses of intermediates are not estimated separately, but are included in the estimates of the vapor losses that occur during dye synthesis and product filtering.

Most of the chemicals with high vapor pressures at room temperature (see Section 3) are chemicals used as solvents or reaction aids. These materials are not incorporated into the dye molecule and are not truly dye intermediates. In general, these chemicals have low melting points and will be transferred as liquids. The scrubber blowdown from the material receiving and handling area could contain these materials and may be a logical sampling point for chemicals of interest (such as formaldehyde). No estimate of losses of these compounds was made because it was difficult to quantify the amounts of material used.

DYE SYNTHESIS

Solid Residues

The major solid residue produced during dye synthesis is the discharge from a filter press if one is used to clarify the diazonium salts and other incomplete dye liquors. Keinath (1976) reported an example of this filtering operation at the Fabricolor facility in Patterson, New Jersey. A filter cake from clarifying a liquor containing benzidine tetrazonium salts (Celite and carbon are used to form the cake) is washed with water, and the washings are transferred to the coupling vessel where the next synthesis step will occur. A sodium hypochlorite solution is added to the filter press to oxidize and bleach any organic material on the filter cake, and the resulting solution is discharged to the process sewer. The filter cake is then removed and transported to a landfill. Although the Fabricolor facility was producing dyes based on benzidine that are not covered in this report, filtration might be required for any azo dye because the reactions that result in insoluble by-products are not restricted to benzidine dyes.

If the above filtering procedure were followed for other diazotized amines, the water washing step would probably remove some organic and water soluble material from the filter cake, although some may remain adsorbed to the carbon. The materials that remain on this filter cake material after water washings are probably the by-products and the azo decomposition products (e.g., as indicated in the previous discussion of dye chemistry, some of these by-products may be N-nitrosamines and polyaryls). If the washed filter cake were removed without further treatment, it might be considered a hazardous material. The sodium hypochlorite solution that is used to treat the filter cake at Fabricolor probably oxidizes some of the organics, but may also produce soluble chlorinated aromatics, some of which may have toxic qualities. Only a small amount of residual organic material is expected to be sorbed to the cake material after this treatment.

Occasionally, a clarification step is required after a coupling reaction. If the decontamination procedure for the filter is the same as described above (washing, followed by oxidation with hypochlorite), the solid residue produced may have little residual organic content. However, if the hypochlorite oxidation step is not used, the filter cake material may contain insoluble by-products of the coupling reactions, including N-nitrosamines and polyaryl compounds.

The solid residues produced by these filtering operations are expected to be small, and have not been quantified. They should, however, be sampled and chemically analyzed to determine if they represent a significant hazard.

Process Wastewater

Process wastewater is produced when reactors are cleaned between dye syntheses. This cleanup water would contain detergents, unreacted intermediates, by-products, and dye. However, cleanup may not occur between every synthesis, because the dyes are sometimes produced in a light-to-dark sequence, which would disguise any carryover from uncleaned or incompletely cleaned equipment. Also, for a major dye or pigment, a train of equipment may be exclusively used for that dye. Thus cleaning frequency may be decreased. Because there was no information on cleanup frequency and no data on the chemical content of cleanup waters, the loss of materials from equipment cleanup was not quantified separately, but instead was included in an overall loss estimate.

Other sources of wastewater from dye synthesis include floor washdown, laundry, worker showers (Keinath, 1976), and blowdown from scrubbers. The amount of material in the combined process wastewater has not been well determined. Lapp's (1979) estimate of a 1% loss based on the raw materials added to the process was used to estimate the loss of intermediates to the process wastewater. These losses would be in the form of unreacted intermediates, by-products, and dye. Because the final product is assumed to be 50% inert salt for a water-soluble dye and 25% inert ingredients for pigments, disperse dyes, and solvent dyes, these losses are equivalent to 0.5% and 0.75%, respectively, based on final product. Because the losses could occur before significant reaction had occurred or after completion of the synthesis or anywhere in between, it is assumed that one-third of the intermediates were lost as intermediates, that one-third were lost in the form of by-products, which include incomplete couplings, and that one-third were lost in the form of the final dye or pigment product. The one-third share of these losses assigned to intermediates was divided by three to obtain an estimate for individual intermediates because three is a typical number of intermediates. A more rigorous approach would be to choose the number of intermediates for each class or dye (i.e., two for monoazo, three for disazo, and so forth) instead of using the "average" of three. However, the emission factor is small compared with other sources of emission, and it was assumed that the above method was satisfactory.

If nitrous acid treatment of the process wastewater, such as was practiced by the Allied Chemical Co. when it was producing benzidine dyes (Keinath, 1976), is used, the estimated loss of intermediates in the process wastewater is probably an overestimate of the amount of the actual intermediates, by-products, and dye released to the process sewer, because chemical changes will occur during treatment. Nitrous oxide treatment will convert amines to diazonium salts, which will then decay to the by-products discussed in Section 3, including replacement of the amine with hydroxide or chloride. Nitrosamines may also be formed. The value may be a reasonable estimate of the total amount of organic material, however, because nitrous acid treatment was not reported to completely oxidize organics to CO_2 and water. Because the extent to which all manufacturers chemically treat process wastewaters was not known, chemical treatment was not assumed for the industry. The overall waste emission estimate for the entire dye or pigment manufacturing process is not sensitive to these assumptions because much larger losses occur later in the process.

Vapor Losses

During dye and pigment synthesis, vapor losses are expected to be small because the reaction temperatures are low and because the physical properties of the chemical intermediates for which data were found indicate that they have low vapor pressures. The vapor pressures for intermediates and by-products for which no data were found are assumed to be low also. Several materials used during dye manufacture do have significant vapor pressures (such as phosgene, formaldehyde, pyridine, and formamide). Many facilities have vents at process vessels that lead to a scrubbing system (Keinath, 1979; DETO, 1980). Again, the scrubber blowdown should be sampled for these types of chemicals if they are of concern. The vapor losses of intermediates were not quantified separately, but were combined with the vapor losses during materials handling and filtration.

PRODUCT FILTRATION

Solid Residues

The solid residues produced during product filtration are dye solids that are spilled during transfer of the press cake to the drying operation or remain as a residual in the filter press. In keeping with the estimates of Lapp (1979), total losses of dye or pigment are assumed to be 1% of the organic dye or pigment, which converts to 0.5% on a final standardized product basis for the water-soluble dyes and 0.75% for pigments and solvent and disperse dyes. Metal losses are estimated as 10% of the dye or pigment losses. These solid materials are assumed to be washed into the process wastewater system so that product filtration does not produce a solid residue directly, although solid residues may result from wastewater treatment.

Process Wastewater

The major contributors to potential discharges of material from filtration operations are the mother liquor and process wastewater from filtration equipment washwaters. The mother liquor will contain unreacted intermediates, terminated coupling products, other by-products (see Section 3), and dye. To calculate the amounts of these materials that might be present, we assumed that 5% excess (molar basis) of each coupling component, with respect to the diazo component, is used during dye or pigment manufacturing. Five percent of the diazo component in each coupling step is assumed to go to by-products, with terminated couplings being the dominant species. Hence, the yield of desired product from each coupling reaction is 95%, based on the diazo component.

The extent of precipitation and efficiency of filtration will determine the amount of dye remaining in the mother liquor. We have assumed that 2% of a soluble dye (standardized dye product basis) remains in the mother liquor because salting out will not make it completely insoluble. This is equivalent to the estimates of 1%-3% made by Lapp (1979). Since pigments and disperse and solvent dyes are insoluble in water, it has been assumed that only traces of these compounds remain in the mother liquor.

The average amount of standardized dye or pigment produced per batch varies between the subclasses. The water-soluble dyes are produced in batches of about 23,000 liters, giving, on the average, 800 kg of filter cake or 1700 kg of standardized product. The water-insoluble compounds are produced in smaller batches of an average 12,000 liters giving about 600 kg of product. These averages were developed from the BIOS (1945) recipes. The amounts of each unreacted intermediate estimated to be in the mother liquor (Appendix B shows the basis for this estimate) are equivalent to 2% of the standardized water-soluble dye products and 3% of the standardized water-insoluble products. These amounts represent a residual concentration for each intermediate in the mother liquor of approximately 1500 ppm for either type of dye.

Because each coupling is assumed to be only 95% complete, the total amount of by-product formed increases with the number of coupling reactions. The total amounts of by-product estimated to be formed when synthesizing monoazo, disazo, trisazo, and polyazo dyes and pigments is shown below. (The details of the estimation procedure are shown in Appendix B.)

	By-Product Concentration in the Mother Liquor (ppm)				As % of Final Standardized Product			
	Monoazo	Disazo	Trisazo	Polyazo	Monoazo	Disazo	Trisazo	Polyazo
Water-soluble dyes	1000	3000	5000	10,000	1.5	4	7.5	15
Pigments or water-insoluble dyes	1500	4000	7500	15,000	2	6	11	22

It is possible that many of the by-products will be insoluble or could be salted out along with the product dye or pigment and that some unreacted intermediates will also salt out when product dyes are precipitated. This means that substantial amounts of these materials could be sold along with the product. However, because no information was found to confirm this level of contamination, it was assumed that all unreacted intermediates and by-products remained soluble in the mother liquor. There is some justification for this assumption since we have assumed that, on a final standardized product basis, 2% of the final dye product remains in solution in the mother liquor. This 2% represents a 4000-ppm concentration of the organic dye molecule, which is probably the most insoluble material present. Each of the unreacted intermediates is present at a level of 1500 ppm, and each by-product is present at levels of only 1000 ppm to 2000 ppm. The concentration of individual by-products was derived from the concentration of total by-products by dividing by the number of major by-products identified in Appendix B. The level of intermediates and by-products in the final product would then be due only to the residual mother liquor remaining in the filter cake before it was dried.

Abrahart (1968) indicates that the residual water content of the filter cake is about 10%, which is about 80 kg or 0.35% of the total mother liquor. 2If an intermediate were present at 1500 ppm in the mother liquor, the residual water in the filter cake would contain 1500 ppm x 80 liters = 0.12 kg of the intermediate. In the final standardized product dye, this 0.12 kg represents about 70 ppm for that intermediate. In a similar manner, the 5000 ppm total of by-products in the mother liquor of a trisazo acid dye would result in about 230 ppm of by-product in the final dye product. The final dye or pigment product could thus contain a total of several hundred parts per million of unreacted intermediates and by-products.

Because the practices used to prepare the metal complexes of dyes vary, it is difficult to quantify the amounts of metal that may be present in process wastewaters from product filtration wastes. Where the complex is prepared by adding metal salts to the organic filter cake and then drying the reaction mixture, the only significant emissions of metal will parallel the emissions of dye, such as spillage of product material during transportation to the product finishing operation. Any excess metal added to promote complete reaction will be sold along with the product. When the complex is prepared in the mother liquor before precipitation and filtration, excess or unreacted metal salts present in the mother liquor would be released to plant wastes along with metal associated with dye that did not precipitate. Additional metal releases would occur along with dye releases from residual filter cake in the press and spills during transfer to the product finishing operation. The actual lo[illegible] metal would be much higher than when only the precipitated dye is met[illegible]

To indicate the [illegible] possible losses, we have assumed that all dyes are complex[illegible] the mother liquor and thereby generated high estimates of me[illegible] for those dyes that are metallized after precipitation and filt[illegible] sed on the recipes that were available, for 1:1 metal complexes, the organic part of the molecule for all metal complex dyes was assumed to have a molecular weight of 450. Since chromium has a molecular weight of 52 and copper has a molecular weight of 62.5, the metal is approximately 10% by weight of the pure dye product even when the chloride anion is included in the final molecular weight. For the more complex dyes with higher molecular weights and the 1:2 complexes, this 10% would represent an overestimate. Since unprecipitated dye concentrations in the mother liquor have been estimated to be 4000 mg/liter, the equivalent metal concentrations would be 400 ppm. Under the acid conditions typically used to precipitate metallized dyes before filtration, this level of metal would be soluble even if it were not complexed with the dye molecule.

Vapor Losses

Vapor losses during filtration would consist primarily of unreacted intermediates and some solvents and reagents because the dye or pigment product and most of the by-products would not have signifcant vapor pressures. Because all the intermediates are also assumed to have low vapor pressures, total vapor losses are estimated to be minimal. Many facilities have dust and vapor control systems that collect the material lost from materials handling, dye synthesis, and the filtration process (DETO, 1980; Keinath, 1976) and process it through a scrubber. Lapp (1979) estimated that during the manufacture of azo dyes based on benzidine, the total losses of benzidine and its congeners to the scrubber system from materials handling, dye synthesis, and filtration was 0.25% of the amount used. It would be reasonable to assume the same level of losses for each other intermediate used. Benzidine dye manufacture should be typical of the whole azo dye industry because the same manufacturing steps and type of facilities are used. On the average, each intermediate (assuming an "average" of three intermediates) represents approximately 17% of the final standardized dye product so that the 0.25% loss of an ingredient can be expressed as 0.04% on a final dye product basis. For pigments and disperse and solvent dyes, this figure is 0.08%. If a plant did not have a scrubber system, dusts and vapors could severely contaminate the work place environment before they were washed into the plant wastewater systems or released to the outside environment.

DRYING, GRINDING, STANDARDIZATION, BLENDING, AND PACKAGING

Solid Residues

Solid residues from the final processing or finishing of dyes and pigments would consist principally of dusts produced during drying, grinding, standardization, blending, and packaging. Most of these dusts will be captured by moving air in a vent or hood system when they are used and would then be removed from the air in a baghouse. Boeniger (1980) details the hood system at two facilities manufacturing dyes and pigments based on benzidine and its congeners. Although the hood systems were not adequate to prevent some exposure to workers, they probably did collect most of the dust. Some of the collected dust in pigment processing was returned to the product.

Lapp (1979) estimated that, during the manufacture of azo dyes based on benzidine and its congeners, 1%-5% of the organic dye is lost during finishing. This can be expressed as 0.5%-2.5% of the final standardized dye product, and it has been assumed that 2% is typical. All azo dyes are assumed to have similar losses because the processing steps are nearly identical. This material will be mostly dust collected in the baghouse at facilities that have good engineering controls.

For dry process azo pigments based on benzidine and its congeners, Lapp (1979) has estimated that 1%-3% of the final product is lost during drying and grinding. We assumed 3% is lost to cover additional losses during standardization and blending. For pigments that are flushed, losses were estimated by Lapp to be 1%-3%, mostly during transfers between equipment and containers. To be conservative, we assumed 3%. For pigment sold as press cake, losses of product were estimated to be 1%, mostly from material transfers. Most of these pigment losses will probably become solid residues that are either collected in the baghosue facilities or swept up from the floor. The average solid waste production is 2.1% of the final pigment product, computed as follows:

(45% dry processed pigment x 3% loss) + (40% flushed pigment x 3% loss x 50% inert) + (15% press cake x 1% loss) = 2.1%.

This estimate is assumed to hold for the solvent and disperse dyes since they are handled in a similar manner. Metal losses are estimated to be 10% of the losses of the dye or pigment that they are complexed with.

Vapor Losses

There are potential vapor emission sources in dye and pigment finishing. The drying operation, which removes the 10% mother liquor in the filter press cake, could also volatilize some of the unreacted intermediates and by-products present. With the exception of a few intermediates such as aniline and ethyl chloride, these materials are known or assumed to have vapor pressures far less than that of water. Therefore, significant volatilization of intermediates, if they were present on the dye or pigment, would not be expected during drying. The second opportunity for unreacted intermediates to volatilize occurs if materials are carried from process to process in open tote boxes. However, very little volatilization is expected because of the low temperatures. Some of the organic vapors from open tote boxes will be entrained in air entering scrubbers or baghouses operated to control emissions at specific processing steps.

The solvents and chemicals other than intermediates used during dye manufacture that are carried to the drying step in the residual mother liquor will be vaporized with the water during the drying step. If processed by a scrubber, the vapors will be collected and contribute to contamination of the process wastewater. If processed through a baghouse, the vapors will probably escape to the atmosphere.

SUMMARY OF AQUEOUS AND SOLID RESIDUE DISCHARGE ESTIMATES

The estimated amounts of intermediates, by-products, and dye or pigment that are discharged by the various operations used in azo dye and pigment manufacturing are summarized in Table 10 for water-soluble dyes and Table 11 for pigments and solvent and disperse dyes. As was discussed in detail previously, these estimates are assumed to be either typical or worst case for the industry and have not taken into account site-specific factors such as the absence or presence of scrubbers on process vents at a particular site. They do not include specific dye or pigment chemistry that might require more or less excess ingredients than assumed or yield more or less by-product; the

Table 10

SUMMARY OF THE ESTIMATED AQUEOUS WASTES AND SOLID RESIDUE PRODUCED BY WATER-SOLUBLE DYE MANUFACTURING OPERATIONS

(All losses are reported as a percentage of the weight of the final marketed product that has been standardized by the addition of inert salts)

	Aqueous Wastes				Solid Residue			
Process Step or Operation	Dye	Inter-mediates (each one)	By-Product	Metal (as the element)	Dye	Inter-mediates	By-Product	Metal (as the element)
Raw material handling	--	a	--	--	--	0.05[b]	--	0.05[b]
Synthesis[c]	0.16	0.06	0.16	0.02	--	--	--	--
Product filtration[d]								
Monoazo	2.5	2	1.5	0.25	--	--	--	--
Disazo			4		--	--	--	--
Trisazo			7.5		--	--	--	--
Polyazo			1.5		--	--	--	--
Air pollution control[e]	--	0.04	--	--	--	--	--	--
Product finishing[f]	--	--	--	--	3	--	--	0.3
Total[g]	2.7	2.1	h	0.27	3	b	0	b

---

[a] Losses were not quantified separately but are included in air pollution control.

[b] Intermediate residue on fiber drums and shipping containers. The estimated loss of each intermediate is this number divided by the number of intermediates in the dye.

[c] Material in wash down of equipment and floors, laundry, and worker showers.

[d] Material in mother liquor and process wastewaters from washdown of the filter press.

[e] Scrubber treating vents and hoods associated with raw material handling, synthesis, and product filtration.

[f] Dusts from drying and grinding collected in a baghouse.

[g] Rounded.

[h] Total depends on subclass.

Table 11

SUMMARY OF THE ESTIMATED AQUEOUS WASTE AND SOLID RESIDUE PRODUCED BY PIGMENT AND SOLVENT AND DISPERSE DYE MANUFACTURING OPERATIONS

(All losses are reported as a percentage of the final marketed product that includes inert ingredients such as oil and filler)

Process Step or Operation	Aqueous Wastes				Solid Residue			
	Insoluble Dye or Pigment	Inter-mediates (each one)	By-Product	Metal (as the element)	Dye or Pigment	Inter-mediates	By-Products	Metal (as the element)
Raw materials handling	--	a	--	--	--	0.075[b]	--	0.075[b]
Synthesis[c]	0.24	0.08	0.24	0.024	--	--	--	--
Product filtration[d]								
Monoazo	0.75	3	2	0.075	--	--	--	--
Disazo			6		--	--	--	--
Trisazo			11		--	--	--	--
Polyazo			22		--	--	--	--
Air pollution control[e]	--	0.08	--	--	--	--	--	--
Product finishing[f] (including baghouse)	--	--	--	--	2.1	--	--	0.21
Total[g]	1	3.1	h	0.1	2.1	b	0	b

---

[a] Losses were not quantified separately, but are included in air pollution control.

[b] Intermediate residue on fiber drums and shipping containers. The estimated loss of each intermediate is this number divided by the number of intermediates in the dye or pigment.

[c] Material from washdown of equipment and floors, laundry, and worker showers. Pigment present will probably be suspended rather than dissolved.

[d] Material in the mother liquor and process wastewater from washdown of the filter press. Pigment present will probably be suspended rather than dissolved.

[e] Scrubber treating vents and hoods associated with raw material handling, synthesis, and product filtration.

[f] Dusts from drying and grinding collected in a baghouse.

[g] Rounded.

[h] Total depends on subclass.

material estimated to be in the aqueous-solid stream is subject to wastewater treatment, as is discussed below.

WASTEWATER TREATMENT

The principal potential source of dye, by-product, or intermediate release to the environment from dye manufacturing operations is the aqueous process wastewater stream. Each dye producer may have a different wastewater treatment system. As discussed previously, some producers use chemical reactions (treatment with nitrous acid) to oxidize the organic compounds in process water generated by equipment washdown, air pollution control scrubbers, worker showers, and laundry preceding discharge of material into the plant sewer (Keinath, 1976). Other producers discharge all process wastewaters directly to sewers and thus to publicly owned treatment works.

Some producers have on-site wastewater treatment plants involving primary, secondary, and tertiary treatment. These treatment plants will all be site-specific designs with site-specific behavior. Games and Hites (1977), for example, have reported plant discharge after secondary treatment of 2200 kg of organics daily from a South Carolina dye manufacturer using eleven million liters of process water per day. The waste before treatment had a chemical oxygen demand (COD) of about 670 ppm. Treatment plant performance averaged about 70% and 80% reduction of COD and BOD (biological oxygen demand) to produce an effluent with a COD of 200 ppm and a BOD of 60 ppm. The plant wastewater treatment system consisted of an equilization pond, a neutralization step, an aerated lagoon with a retention time of less than 5 days, and two large settling ponds with a retention time of 19 days.

Anliker and Clark (1979) have reported an effluent concentration before treatment from a dyestuff manufacturer as 900-4000 ppm BOD and 600-1000 ppm total organic carbon (TOC). Other documents (such as EPA, 1975) give wastewater flows at six different dye manufacturing plants as 33, 114, 175, 200, 800, and 1800 liters/kg finished product. Sampling of these wastestreams gave the following ranges: 200-5000 ppm BOD, 1200-4000 ppm COD, and 500-2000 ppm TOC.

Keinath (1976) reports that typical wastewater flows (including mother liquor) are 250-750 liters/kg finished product. Based on the aqueous emission levels indicated in Tables 10 and 11 these wastewater flows might have 25-100 ppm of each unreacted intermediate and 30-100 ppm of by-products for a monoazo dye and 200-900 ppm of by-products for a polyazo dye. Dye concentrations might be 10 to 100 mg/liter, and if metals were used their concentration could be 3 to 10 mg/liter. For example, manufacture of 1 kg of standardized monoazo dye is estimated to release 0.017 kg of by-products to the process sewer. In 250 liters of water, this material would have a concentration of 70 mg/liter.

A complete assessment of emissions to all media (air, water, and solid) would have to consider each manufacturer's plant individually in terms of plant operation, wastewater treatment plant operation, and the specific dyes produced. This is beyond the scope of the current study, which necessarily must neglect site-specific factors. Consequently, the behavior of the organics that might be present in wastewaters is discussed with respect to potential wastewater treatment operations. We focused on biological treatment processes because these will be present either at most manufacturing sites or at the municipal wastewater treatment systems receiving the wastewater from the manufacturing site.

The behavior of the materials during wastewater treatment is discussed in terms of the following four classes of material thought to be present:

(1) Unreacted organic intermediates

(2) Product dye

(3) Reaction by-products

(4) Metals.

Unreacted Intermediate

Physical properties data and biotreatability information were found for only a few intermediates. These data indicated that the intermediates have moderate to high solubility in water and weak adsorption to organic material (low K_{oc}). Therefore, it seems reasonable to assume that these materials will not partition strongly onto sludge during wastewater treatment. Some compounds, such as phenol, are readily biodegradable in adapted systems. Some of the sulfonated aromatics are resistant to degradation (Meyer et al., 1979). In this study, biodegradation was assumed not to occur because the episodic nature of discharges that result from the batch nature of dye manufacture does not permit an adapted culture to develop. However, an adapted culture may develop for intermediates common to many different dyes and pigments such as β-naphthol, aniline, or phenol.

Product Dye

The sources of information on biodegradation of dyes* indicated that biodegradation of dyes and pigments does not occur to a significant extent in aerobic wastewater treatment processes. In particular, biotreatment systems were not found to acclimate to dyes (ADMI, 1973), and some systems may be inhibited by some dyes (ADMI, 1973). Brown et al. (1981) have shown that the majority of dyestuff types (including many azo dyes) are not likely to be significantly toxic to aerobic sewage treatment processes. The pigments are, in general, not readily biodegradable in aerobic systems (Anliker and Clarke, 1979). Several of these studies also indicate that, at sewage bacteria concentrations typical of wastewater treatment facilities, adsorption would not be significant except for some direct dyes that have an affinity for bacteria.

---

*ADMI (1973), Keinath (1976), ETAD (1980), Hitz et al. (1978), Dieckhues (1961), Tincher (1978), Baird et al. (1977), Porter (1973), Dubin and Wright (1975), Tabak and Barth (1978), Urushigawa and Yonezawa (1977), Kappeler et al. (1978), Flege (1970), Idaka et al. (1978), Meyer et al. (1979), Brown et al. (1981).

The removal of color from the waste stream occurs when the soluble dye is absorbed on the bacterial sludge or the insoluble dyes and pigments settle to the bottom of a nonagitated basin or lagoon. Because the dyes are designed to resist oxidative degradation, it is not likely that the aerobic biological process would have much effect on them.

Reaction By-Products

Only a few of the many by-products possible based on theoretical chemistry may have been identified by actual chemical analysis. As discussed in Section 3, the diazotized amine may decompose (the diazonium group being replaced by a hydroxide or chloride). The by-products of more complex dyes will include these types of compounds plus some coupled products. N-nitrosamines may be present in the process wastewater.

Little information was found on the physical or biological properties of these compounds, so it is difficult to determine how wastewater treatment would affect them. Substantial rates of biodegradation are not expected. Meyer (1979) found that, under aerobic conditions, the biodegradation rate of derivatives of the simple azo compound, phenylazonaphthalene, was affected by the nature of the substituents present (e.g., SO_3H and COOH). Double substitution was found to inhibit the degradation, and, whenever a sulfonic acid group was present, the degradation was significantly reduced in all cases studied.

For this assessment, we have assumed that by-products are only slowly biodegraded and not strongly adsorbed to sediment or biological material. The previously cited studies have shown that the dyes themselves are not strongly sorbed under the conditions of wastewater treatment, so related but smaller molecules are not likely to be either.

Metals

The fate of the metals used to produce premetallized dyes depends on their chemical state when they enter the treatment system. Metals that have not reacted with dye molecules, either because they were added in excess or because the metallization reaction was incomplete, should be removed by probable treatment processes, including neutralization using lime and biological treatment. The metals (Cr, Co, Cu, Ni) are soluble under acid conditions, but become insoluble under moderately basic conditions. Chromium, for example, has a solubility of 6 mg/liter at pH 7, a higher solubility at pH

6, and a solubility of less than 0.1 mg/liter at pH 8 to 9. Solubility increases again at pH values above 9 (Patterson and Minear, 1971). Copper has its minimum solubility in the pH 9-10 range, whereas for nickel the solubility minimum is at pH 10. The insoluble species is the metal hydroxide. Cobalt is assumed to behave similarly to chromium.

Patterson and Minear (1971) and Hanson (1979) report actual treatment results where metal levels as high as several hundred ppm were reduced to 1-2 ppm by lime neutralization and settling. These results are not as good as might be expected based on solubility because some of the metal hydroxide precipitate is colloidal and does not settle well.

Biological processes remove metal salts from solution. Peck and Gorton (1977), and Vigon et al. (1977) reviewed the behavior of heavy metals in activated sludge systems. Their results indicate that from 50% to 60% removal of Cu, Ni, Cu, and Co might be expected in wastewaters containing ppm levels of metal. The metals are adsorbed on the biological solids. Two factors are probably involved in this adsorption. The sludge may physically collect colloidal metal hydroxide particles that are too small to settle by themselves. There could also be ionic interactions with constituents in bacterial cell walls.

The estimates of waste emissions from dye manufacture in this study do not assume that excess metal is added to the reaction mixture. Therefore, the 3-10 ppm of metal estimated to be in the plant wastewater is assumed to be in the form of the dye-metal complexes. The majority of the metallized dyes (by production volume) are acid dyes that are acid insoluble but soluble in neutral and basic solutions. Because these dyes are designed to be colorfast, which means that the dye-metal complex is strongly bonded to the fiber, it is not believed that the mildly alkaline conditions used for neutralization during wastewater treatment will free the metal from the dye-metal complex. Therefore, neutralization is not expected to cause much metal precipitation either as an insoluble dye-metal complex or the insoluble metal hydroxide. The dye-metal complex is not expected to adsorb strongly to the calcium hydroxide and calcium carbonate sludge produced by neutralization because acid dyes are designed to bond ionically to positively charged amine groups in wool protein. The neutralization sludge particles will most likely have a negative surface charge. Even so, the neutralization sludge will probably contain some dye. [This conclusion is based on Keinath's (1976) observation that lime neutralization sludge did adsorb some of the dye intermediate benzidine from wastewaters and on Tincher's (1978) finding of acid azo dyes on river muds downstream from carpet mills.]

Biological treatment is not expected to be effective in removing metals in soluble metallized dyes from wastewater because biological treatment is not effective in removing the dyes themselves. However, as discussed when considering biological treatment of dyes, some adsorption to biological solids is expected.

Some of the metal complexes are disperse dyes and pigments. These would be present in plant wastewaters as suspended solids that would be removed by a neutralization and settling treatment.

Summary of Results of Wastewater Treatment

The previous discussion has shown that the behavior of dye intermediates, by-products, dyes, and metals is incompletely understood with respect to biodegradability and sorption onto solids. In addition, even compounds that are biodegradable may not be degraded in a wastewater treatment system because of the episodic nature of discharges due to the batch production of dyes. The interval between batches may be long enough for the bacteria in the system to lose the ability to degrade a particular compound. Compounds may also be present that interfere with biodegradation. As a way of dealing with this uncertainty as to treatability of dye plant aqueous wastes, we have assumed that biological wastewater treatment is ineffective. Consequently, a majority of the material released to process sewers is assumed to be released to the environment. Furthermore, although it is recognized that some components in the wastewater are more likely to be found on the solids produced by treatment than in the aqueous phase, all material emissions are considered to be in a joint aqueous-solid phase. This assignment actually reflects the expectation that every chemical in process wastewater will be found at some concentration in both the solid and aqueous phases produced by wastewater treatment.

SECTION 6

SOLID RESIDUE AND AQUEOUS WASTE PRODUCTION

The amounts of solid residue and aqueous wastes produced by azo dye and pigment manufacture were estimated for each dye and pigment using the methodology developed in Section 5. For this analysis, "solid residue" includes only the identifiable solid material associated with shipping container disposal and dye or pigment fines collected in baghouses. The "aqueous waste" is the estimated amount of material in dye or pigment plant process wastewater before the final wastewater treatment. Wastewater treatment, which may take place at the manuafacturing site or a municipal wastewater treatment system, is assumed to involve sedimentation followed by biological treatment and final clarification. These treatments are assumed to be ineffective in reducing the amount of each compound by degradation, but will partition the material between wastewater treatment solids and the aqueous effluent. The wastewater treatment solids will probably be disposed in a landfill and the effluent eventually discharged to surface waters after treatment. Because it was impossible to predict what the partitioning of intermediates between the wastewater treatment solids and the aqueous effluent would be, each aqueous emission was considered to be in a joint "aqueous-solid waste" stream.

It is important to realize that dyes and by-products may be on the wastewater treatment solids because if these solids are placed in a landfill, they will be in an anaerobic environment where reductive reactions can take place. Diekhues (1961) found, for a variety of azo dyes, that reductive splitting of the azo linkage occurred. This means that the dye intermediates could be released in a landfill even from dye wastes that did not originally contain these materials in a free state.

Table 12 summarizes the estimated emissions of dye or pigment, intermediates, and by-products for azo dyes and pigments where the intermediates could be identified from information in Colour Index (The Society of Dyers and Colourists, 1980). For the dyes and pigments without C.I. numbers, the emissions could not be estimated because the intermediates are not identified. The dyes and pigments in the table are listed by C.I. number. Table 13 lists the chemical name for the intermediates with the common names shown in Table 12. Letter codes (defined in Table 14) indicate the producers for each dye or pigment. Tables 15 through 19 list the dyes and pigments that each producer makes. The identity and corporate ownership of the producers is based on 1978 information. Since it was compiled, several dye production facilities or dye lines have been sold. Sales that were announced in trade journals are shown as footnotes in Table 14. A systematic search was not made to verify that all such sales have been listed, so the table may not be complete.

The amount of each of the intermediates in the solid residue or aqueous-solid waste stream was obtained by multiplying the dye or pigment production value from Table 1 by the emission factors in Table 10 or Table 11. For example, for Disperse Orange 3 (which is the second dye in Table 12), the solid residue due to materials handling of each intermediate was obtained by multiplying the production value of 21.4 metric tons for the standardized dye product by the emission factor 0.075% to obtain the estimate of 16 kg/yr. This value was then divided by the number of intermediates (2) to give 8 kg/yr as the amount of each of the intermediates aniline and p-nitroanitine in the solid residue stream. This procedure was followed for each dye and pigment. Each organic intermediate and metal salt was counted, but phosgene and ethyl chloride were not because of their low molecular weight contribution to the final dye product. For dyes and pigments where production levels were reported in public sources only as greater than some lower limit, the lower limit was used because there was no way to estimate the actual amount produced.

The esterifying components and condensation components used in the production of several dyes do not become part of the dye molecule via an azo linkage. For these components it is assumed that no excess reactant is required. When these were solids, the only significant losses were assumed to be the solid residue from materials handling.

The estimated discharges of each intermediate from specific dye and pigment manufacturing were summed to indicate the total amount, on an industry-wide basis for the azo dyes and pigments covered in this study, of each intermediate estimated to be in solid residue and in the aqueous-solid waste streams. These industry-wide emission estimates (for those intermediates with estimates greater than 50 kg/yr) are shown in Table 20, listed in the order of the amount estimated to be in the solid residue. These industry-wide estimates could overstate the emissions of some intermediates if industry practice is different from the assumptions developed in Section 5. The estimates also probably understate the emissions for the intermediates used in azo dyes and pigments where only the lower production limit was known. It is possible that if actual production values were known for these dyes and pigments and used to estimate emissions, some of the intermediate emissions now judged to be minor could become more important.

Based on the estimates in Table 12, the industry-wide total amount of identified organic intermediates in the solid residue from the manufacture of the azo dyes and pigments covered in this study is 13.6 mt/yr. The total amount of dye or pigment in the solid residue (obtained by summing the values for each dye and pigment in Table 12) is estimated to be 330 mt/yr, which makes the dyes and pigments themselves the more significant synthetic organic component of the total solid residue stream. The total amount, industry-wide, of intermediates estimated to be in the aqueous-solid waste is 630 mt/yr. This aqueous-solid waste is also estimated to contain 330 mt/yr of dyes and pigments and 640 mt/yr of reaction by-products. It is interesting to note that if only 2.5% of the intermediates estimated to be in the aqueous-solid stream were actually adsorbed on wastewater treatment solids, then the amount of intermediates estimated to be in the solid residue from dye and pigment manufacture would double. In a similar manner, if only 10% of the by-products were to be adsorbed on wastewater treatment solids then these by-products would be a significant fraction of the synthetic organic chemicals contained in the solid residue stream.

The intermediates in Table 20 with the largest estimated emissions are mostly associated with the dyes and pigments that are produced in the largest volume. The ten largest volume dyes and pigments are produced by an average of ten companies. Thus these intermediates should not be site-specific and should be detectable at most major production facilities. Several intermediates, such as 2-amino-1-naphthalene sulfonic acid and 6-amino-m-toluene sulfonic acid, may be used in only one major dye or pigment; thus their release may be periodic. However, 2-naphthol is used in many dyes and pigments and it should be detectable in the process wastewaters on a nearly continuous basis. 2-Naphthol and 3-hydroxy-2-naphthoic acid account for nearly 50% of the combined intermediates estimated to be in the aqueous-solid waste and thus should be present at levels below 100 ppm in the total combined wastewater before wastewater treatment.

Table 12

ESTIMATED WASTES PRODUCED IN MANUFACTURING AZO DYES AND PIGMENTS OTHER THAN THOSE BASED ON BENZIDINE AND ITS CONGENERS

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released[a] (kg/yr) Solid Residue	Quantity Released[a] (kg/yr) Waste-water
[illegible]	11000	Solvent Yellow 1	>2.3	Solvent Yellow 1	48	23
				Aniline	1.7	--
				By-products	0	51
AC ALT ATL TRC	11005	Disperse Orange 3 Solvent Orange 9	21.4	Disperse Orange 3	450	214
				p-Nitroaniline	8	--
				Aniline	8	660
				By-products	0	470
ACY	11014	Basic Red 30	>2.3	Basic Red 30	69	61
				2-Amino-N-methypyridinium	0.6	--
				Salt	0.6	48
				Aniline		
				By-products	0	39

[a] An entry of -- means that none of this material is estimated to be released to the waste water.
An entry of 0 means that only traces of this material are estimated to be released to the solid waste.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production Metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
ACY PSC	11021	Solvent Yellow 56	>4.5	Solvent Yellow 56	94	45
				Aniline	1.7	--
				N, N-Diethylaniline	1.7	140
				By-products	0	99
ACY	11043	Basic Violet 18	>2.3	Basic Violet 18	69	61
				2-Amino-N-methylpyridinium Salt	0.6	--
				N,N-Dimethylaniline	0.6	48
				By-products	0	39
ACY BAS GAF	11052	Basic Blue 54	>6.8	Basic Blue 54	204	180
				2-Amino-6-methoxy-3-methylbenzothiazole	1.7	--
				N,N-Dimethylaniline	1.7	143
				Methyl sulfate[b]	--	--
				By-products	0	116

[b] The dye is sold as the quaternary ammonium methosulfate. No estimation of the quantity of the methyl sulfate intermediate was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
TRC	11055	Basic Red 22	>2.3	Basic Red 22	69	61
				5-Amino-1, 4-dimethyl-1H-1,2,4-triazole	0.6	--
				N,N-Dimethylaniline	0.6	48
				By-products	0	39
DUP	[illegible]	Basic Orange 24	>2.3	Basic Orange 24	69	61
				(p-Aminobenzoylmethyl) trimethylammonium chloride	0.6	--
				3-(N-Methylanilino) propionitrile	0.6	48
				By-products	0	39
DUP HST VPC	11077	Disperse Blue 165	>6.8	Disperse Blue 165	143	68
				2-Amino-5-nitro-isophthalonitrile	2.6	--
				m-Diethylaminoacetanilide	2.6	211
				By-products	0	150
AAG ALT ICI MAY TRC	--	Disperse Blue 79	1284	Disperse Blue 79	27000	12840
				2-Bromo-4,6-dinitroaniline	480	--
				m-Diethanolamino-p-methoxyacetanilide	480	39800
				By-products	0	28200

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
ATL BAS DUP GAF VPC	11085	Basic Red 18	147.3	Basic Red 18	4420	3980
				2-Chloro-4-nitroaniline	37	--
				[2-(N-ethylanilino)ethyl] trimethyl ammonium salt	37	3090
				By-products	0	2500
DUP	11087	Basic Yellow 15	>2.3	Basic Yellow 15	69	61
				(p-Aminobenzoylmethyl) trimethylammonium chloride	0.6	--
				3-(2-Chloroanilino) propionitrile	0.6	48
				By-products	0	39
ATL EKT	11100	Disperse Orange 5	>4.5	Disperse Orange 5	95	45
				2,6-Dichloro-4-nitroaniline	1.7	--
				2-(N-Methylanilino)ethanol	1.7	140
				By-products	0	99

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
AC EKT ACY GAF ATL SDH BAS TRC DUP	11110	Disperse Red 1	174.1	Disperse Red 1	3660	1740
				p-Nitroaniline	66	--
				2-(N-Ethylanilino)ethanol	66	5400
				By-products	0	3830
ATL BAS GAF	11115	Disperse Red 13	>6.8	Disperse Red 13	143	68
				2-Chloro-4-nitroaniline	2.5	--
				2-(N-Ethylanilino)ethanol	2.5	211
				By-products	0	150
BAS TRC	11116	Disperse Red 73	>4.5	Disperse Red 73	95	45
				2-Amino-5-Nitrobenzonitrile	1.7	--
				3-(N-Ethylanilino) propionitrile	1.7	140
				By-products	0	99

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Wastewater
[illegible]	11117	Disperse Red 90	>2.3	Disperse Red 90	48	23
				2-Amino-5-nitrobenzonitrile	0.8	--
				3-(N-2-Cyanoethylanilino) propionic acid methylester	0.8	71
				By-products	0	51
ATL FAB TRC	11119	Disperse Orange 30	>6.8	Disperse Orange 30	143	68
				2,6-Dichloro-4-nitroaniline	2.6	--
				3-(N-2-Hydroxyethylanilino) propionitrile, acetate ester	2.6	211
				By-products	0	150
BAS FAB	--	Disperse Red 54	>4.5	Disperse Red 54	95	45
				2-Chloro-4-nitro-aniline	1.7	--
				3-(N-2-Hydroxyethyl-anilino)-propionitrile, acetate ester	1.7	140
				By-products	0	99
AC	11150	Disperse Red 7	>2.[illegible]	Disperse Red 7	48	23
				p-Nitroaniline	0.8	--
				2,2′-(m-Chlorophenylimino) diethanol	0.8	71
				By-products	0	51

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
AC ALT ATL BUC HST ICI SDC TRC	11152	Disperse Brown 1	18.2	Disperse Brown 1	382	182
				2,6-Dichloro-4-nitroaniline	6.8	--
				2,2′-(m-Chlorophenylimino) diethanol	6.8	564
				By-products	0	400
BAS TRC	11154	Basic Blue 41	>4.5	Basic Blue 41	135	120
				2-Amino-6-methoxy-3-methyl-benzothiazole	1.1	--
				N-methyl-N-(2,3-dimethoxy-propyl) aniline	1.1	95
				By-products	0	77
PSC	11160	Solvent Yellow 3	>14	Solvent Yellow 3	290	140
				o-Toluidine	11	--
				By-products	0	314

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
AC	11210	Disperse Red 17	77.3	Disperse Red 17	1620	77
ALT				p-Nitroaniline	29	--
BAS				2,2′-(m-Tolylimino)diethanol	29	2400
EKT						
GAF						
TRC						
				By-products	0	1700
AC	11215	Disperse Red 5	36.4	Disperse Red 5	764	364
ALT		Solvent Red 117		2-Chloro-4-nitroaniline	14	--
HSH				2,2′-(m-Tolylimino)diethanol	14	1130
				By-products	0	800
ALT	11227	Disperse Orange 25	325.5	Disperse Orange 25	6840	3260
DUP				p-Nitroaniline	122	--
EKT				3-(N-Ethylanilino)-propionitrile	122	10100
TRC						
VPC						
				By-products	0	7160

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
AC ALT EKT TRC	11228	Disperse Red 65	104.5	Disperse Red 65	2190	1050
				2-Chloro-4-nitroaniline	36	--
				3-(N-Ethyl-m-toluidino)-propionitrile	36	3240
				By-products	0	2300
ACY ATL BAS DUP GAF PSC TRC	11270 11270:1	Basic Orange 2 Solvent Orange 3	283.6	Basic Orange 2	8510	7650
				Aniline	71	--
				m-Phenylenediamine	71	5960
				By-products	0	4820
ACY GAF PSC TRC	11320 11320:1	Basic Orange 1 Solvent Orange 4	94.1	Basic Orange 1	2820	2540
				Aniline	24	--
				Toluene-2,4-diamine	24	1980
				By-products	0	1600

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
AC	11365	Disperse Black 1	>5	Disperse Black 1	100	50
				p-Nitroaniline	1.8	--
				1-Naphthylamine	1.8	150
				By-products	0	110
BAS	11460	Basic Red 29	>5	Basic Red 29	150	130
				2-Amino-3-methylthiazole	1.2	--
				1-Methyl-2-phenyl-1H-indole	1.2	100
				By-products	0	90
ACY BAS	11480	Basic Yellow 24	>4.5	Basic Yellow 24	135	120
				2-Amino-3-methylbenzothiazol	1.1	--
				1,2,3-Trimethyl-2H-benzimidazole	1.1	95
				Methyl sulfate[c]	--	--
				By-products	0	190

[c] The dye is sold as the quaternary ammonium methosulfate. No estimation of the quantity of the methyl sulfate intermediate was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
HPC KCW	11660	Pigment Yellow 5	>0.9	Pigment Yellow 5	19	9
				o-Nitroaniline	0.4	--
				Acetoacetanilide	0.4	28
				By-products	0	20
HPC	11670	Pigment Yellow 6	>0.5	Pigment Yellow 6	10	5
				4-Chloro-2-nitroaniline	0.2	--
				Acetoacetanilide	0.2	15
				By-products	0	11
AMS DUP GLX HPC HSC HRC HSH HST KCW KON S SDH SNA	11680	Pigment Yellow 1	199.5	Pigment Yellow 1	4190	2000
				2-Nitro-p-toluidine	75	--
				Acetoacetanilide	75	6180
				By-products	0	4390

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
BNS HSH HPC HST HRC KCW HSC KON	11710	Pigment Yellow 3	66.4	Pigment Yellow 3	1390	664
				4-Chloro-2-nitroaniline	25	--
				o-Chloroacetoacetanilide	25	2060
				By-products	0	1460
HST	11720	Pigment Yellow 9	>0.5	Pigment Yellow 9	10	5
				2-Nitro-p-toluidine	0.2	--
				o-Acetoacetotoluidide	0.2	15
				By-products	0	11
HRC KCW	11725	Pigment Orange 1	>0.9	Pigment Orange 1	19	9
				2-Nitro-p-anisidine	0.4	--
				o-Acetoacetotoluidide	0.4	28
				By-products	0	20

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
KCW	11727	Pigment Yellow 98	>0.5	Pigment Yellow 98	10	5
				4-Chloro-2-nitroaniline	2	--
				4-Chloro-o-acetoaceto-toluidide	2	15
				By-products	0	11
KCW	11730	Pigment Yellow 2	>0.5	Pigment Yellow 2	10	5
				4-Chloro-2-nitroaniline	0.2	--
				2,4-Acetoacetoxylidide	0.2	15
				By-products	0	11
HPC HRC HSH HST SNA	11738	Pigment Yellow 73	245.5	Pigment Yellow 73	5160	2455
				4-Chloro-2-nitroaniline	92	--
				o-Acetoacetanisidide	92	7610
				By-products	0	5400

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
HRC HSH SNA	11740	Pigment Yellow 65	>50	Pigment Yellow 65	1050	500
				2-Nitro-p-anisidine	18	--
				o-Acetoacetanisidide	18	1550
				By-products	0	1100
DUP HSH GLX HST HPC SDH HRC SNA HSC VPC	11741	Pigment Yellow 74	588.2	Pigment Yellow 74	12400	5880
				4-Nitro-o-anisidine	220	--
				o-Acetoacetanisidide	220	18200
				By-products	0	12900
S	11765	Pigment Yellow 49	>0.5	Pigment Yellow 49	10	5
				4-Chloro-o-toluidine	0.2	--
				4'-Chloro-2',5'-dimethoxy-acetoacetanilide	0.2	15
				By-products	0	11

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
HST	11767	Pigment Yellow 97	>0.5	Pigment Yellow 97	10	5
				4-Amino-2,5-dimethoxybenzene-sulfonanilide	0.2	--
				4'-Chloro-2',5'-dimethoxy-acetoacetanilide	0.2	15
				By-products	0	11
HPC	11770	Pigment Yellow 75	>0.5	Pigment Yellow 75	10	5
				4-Chloro-2-nitroaniline	0.2	--
				p-Acetoacetophenetidide	0.2	15
				By-products	0	11
AC ALT EKT HSH TRC	11855	Disperse Yellow 3 Solvent Yellow 77	>95	Disperse Yellow 3	2000	950
				p-Aminoacetanilide	36	--
				p-Cresol	36	2900
				By-products	0	2100

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
ACY	12055	Solvent Yellow 14	173.2	Solvent Yellow 14	3640	1730
ATL				Aniline	65	--
DUP				2-Naphthol	65	5370
PSC						
VPC				By-products	0	3810
HPC	12060	Pigment Orange 2	>5	Pigment Orange 2	100	50
KCW				o-Nitroaniline	1.8	--
UHL				2-Naphthol	1.8	150
				By-products	0	110
CGY	12070	Pigment Red 1	>2.7	Pigment Red 1	57	27
HSH				p-Nitroaniline	1	--
SDH				2-Naphthol	1	84
KCW						
				By-products	0	59

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production Metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
ACY	12075	Pigment Orange 5	309.1	Pigment Orange 5	6490	3090
HPC				2,4-Dinitroaniline	116	--
HSC				2-Naphthol	116	9580
HSH						
HST				By-products	0	6800
SDH						
SNA						
ACY	12085	Pigment Red 4	49.5	Pigment Red 4	1040	495
AMS				2-Chloro-4-nitroaniline	18	--
HPC				2-Naphthol	18	1530
HSC						
KON				By-products	0	1090
MRX						
SDH						
UHL						
DUP	12090	Pigment Red 6	10.5	Pigment Red 6	220	105
HSH				4-Chloro-2-nitroaniline	4	--
KCW				2-Naphthol	4	325
KON						
				By-products	0	231

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
PSC	12100	Solvent Orange 2	>2.3	Solvent Orange 2	48	23
				o-Toluidine	0.8	--
				2-Naphthol	0.8	71
				By-products	0	5
ACY KCW CIK KON DUP MRX HPC SDH HSC SNA HSH UHL	12120	Pigment Red 3	485.9	Pigment Red 3	10200	4859
				2-Nitro-p-toluidine	182	--
				2-Naphthol	182	15100
				By-products	0	10700
ACY ATL PSC	12140	Solvent Orange 7	>6.8	Solvent Orange 7	140	68
				2,4-Xylidine	2.6	--
				2-Naphthol	2.6	210
				By-products	0	150

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
PSC	12150	Solvent Red 1	>2.3	Solvent Red 1	48	23
				o-Anisidine	0.8	--
				2-Naphthol	0.8	71
				By-products	0	51
BCC	12156	Solvent Red 80	>2.3	Solvent Red 80	48	23
				2,5-Dimethoxyaniline	0.8	--
				2-Naphthol	0.8	71
				By-products	0	51

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
BNS	12300	Pigment Red 21	>5	Pigment Red 21	100	50
				o-Chloroaniline	1.8	--
				3-Hydroxy-2-naphthanilide	1.8	150
				By-products	0	110
HPC HRC HSH KCW S	12310	Pigment Red 2	23.2	Pigment Red 2	487	232
				2,5-Dichloroaniline	8.5	--
				3-Hydroxy-2-naphthanilide	8.5	719
				By-products	0	510
ACY DUP GLX HPC KCW MRX SNA	12315	Pigment Red 22	35.5	Pigment Red 22	745	355
				5-Nitro-o-toluidine	14	--
				3-Hydroxy-2-naphthanilide	14	1100
				By-products	0	781

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
GLX IND	12320	Pigment Red 32	>0.9	Pigment Red 32	19	9
				3-Amino-p-anisanilide	0.4	--
				3-Hydroxy-2-naphthanilide	0.4	28
				By-products	0	20
ACY BUC DUP GLX HPC HSH IND KCW ROM SDH UHL	12355	Pigment Red 23	200.0	Pigment Red 23	4200	2000
				5-Nitro-o-anisidine	75	--
				3-Hydroxy-3'-nitro-2-naphthanilide	75	6200
				By-products	0	4400
ROM SDH	12360	Pigment Red 31	>0.9	Pigment Red 31	19	9
				3-Amino-p-anisanilide	0.4	--
				3-Hydroxy-3'-nitro-2-naphthanilide	0.4	28
				By-products	0	20

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Wastewater
HST	12367	Pigment Orange 38	>0.5	Pigment Orange 38	10	5
				3-Amino-4-chlorobenzamide	0.2	--
				4'-Acetamido-3-hydroxy-2-naphthanilide	0.2	15
				By-products	0	11
HPC HST	12370	Pigment Red 112	>0.9	Pigment Red 112	19	9
				2,4,5-Trichloroaniline	0.4	--
				3-Hydroxy-2-naphtho-o-toluidide	0.4	28
				By-products	0	20
ACY BNS HPC ICC ROM SNA UHL	12390	Pigment Red 17	41.4	Pigment Red 17	870	414
				5-Nitro-o-toluidine	16	--
				3-Hydroxy-2-naphtho-o-toluidide	16	1280
				By-products	0	911

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
HPC KCW	12395	Pigment Red 13	>0.9	Pigment Red 13	19	9
				2-Nitro-p-toluidine	0.4	--
				3-Hydroxy-2-naphtho-o-toluidide	0.4	28
				By-products	0	20
HST S	12420	Pigment Red 7	>0.9	Pigment Red 7	19	9
				4-Chloro-o-toluidine	0.4	--
				4'-Chloro-3-hydroxy-2-naphtho-o-toluidide	0.4	28
				By-products	0	20
HPC HST MRX	12460	Pigment Red 9	>10	Pigment Red 9	210	100
				2,5-Dichloroaniline	3.8	--
				3-Hydroxy-2-naphth-o-anisidide	3.8	310
				By-products	0	220

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
HST	12465	Pigment Red 15	>0.5	Pigment Red 15	10.	5
				4-Chloro-2-nitroaniline	0.2	--
				3-Hydroxy-2-naphth-o-anisidide	0.2	15
				By-products	0	11
HST	12467	Pigment Red 188	>0.5	Pigment Red 188	10	5
				2-Amino-4-(2,5-dichlorophenylcarbamoyl) benzoic acid, methyl ester	0.2	--
				3-Hydroxy-2-naphtho-o-anisidide	0.2	15
				By-products	0	11
HST S	12475	Pigment Red 170	>0.9	Pigment Red 170	19	9
				p-Aminobenzamide	0.4	--
				3-Hydroxy-2-naphtho-o-phenetidide	0.4	28
				By-products	0	20

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
DUP	12476	Disperse Red 220	>2.3	Disperse Red 220	48	23
				4-Chloro-o-toluidine	0.8	--
				3-Hydroxy-2-naphtho-o-phenetidide	0.8	71
				By-products	0	51
S	12480	Pigment Brown 1	>0.5	Pigment Brown 1	10	5
				2,5-Dichloroaniline	0.2	--
				3-Hydroxy-2',5'-dimethoxy-2-naphthanilide	0.2	15
				By-products	0	11
HST	12485	Pigment Red 146	>5	Pigment Red 146	100	50
				3-Amino-p-anisanilide	1.8	--
				4'-Chloro-3-hydroxy-2',5'-dimethoxy-2-naphthanilide	1.8	150
				By-products	0	110

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
GAF GLX HPC HSH ROM S	12490	Pigment Red 5	25.9	Pigment Red 5	544	259
				N',N'-Diethyl-4-methoxy-metanilamide	9.7	--
				5'-Chloro-3-hydroxy-2',4'-dimethoxy-2-naphthanilide	9.7	803
				By-products	0	570

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
PSC	12700	Solvent Yellow 16	>2.3	Solvent Yellow 16	48	23
				Aniline	0.8	--
				3-Methyl-1-phenyl-5-pyrazolone	0.8	71
				By-products	0	51
HSH KON	12705	Pigment Yellow 60	>0.9	Pigment Yellow 60	19	9
				o-Chloroaniline	0.4	--
				3-Methyl-1-phenyl-5-pyrazolone	0.4	28
				By-products	0	20
BAS	12715	Solvent Red 8	>2.3	Solvent Red 8	48	23
				2-Amino-5-nitrophenol	0.6	--
				3-Methyl-1-phenyl-5-pyrazolone	0.6	71
				Chromium (Cr^{+3})	5.4	2.3
				Formamide[d]	--	--
				By-products	0	51

[d] The dye is heated with chromium formate in formamide solution. No estimation of the quantity of this solvent was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
VPC	12770	Disperse Yellow 4	>2.3	Disperse Yellow 4	48	23
				Aniline	0.8	--
				2,4-Quinolinediol	0.8	71
				By-products	0	51
DUP HPC	12775	Pigment Green 10	>0.9	Pigment Green 10	17	9
				p-Chloroaniline	0.2	--
				2,4-Quinolinediol	0.2	28
				Nickel (Ni^{+2})	1.1	0.9
				By-products	0	20

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Wastewater
ATL	13025	Acid Orange 52	>2.3	Acid Orange 52	69	61
				Sulfanilic acid	0.6	--
				N,N-Dimethylaniline	0.6	48
				By-products	0	39
BAS DUP TRC	13065	Acid Yellow 36	>6.8	Acid Yellow 36	200	180
				Metanilic acid	1.7	--
				Diphenylamine	1.7	140
				By-products	0	120
ACY	13080	Acid Orange 5	>2.3	Acid Orange 5	69	61
				Sulfanilic acid	0.6	--
				Diphenylamine	0.6	48
				By-products	0	39

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
AC	13091	Acid Orange 1	>2.3	Acid Orange 1[e]	69	61
				Sulfanilic acid	0.6	--
				Diphenylamine	0.6	48
				By-products	0	39
AC	13095	Acid Yellow 63	>2.3	Acid Yellow 63	69	61
				Sulfanilic acid	0.6	--
				Diphenylamine	0.6	48
				By-products	0	39
AC	13150	Acid Orange 50	>2.3	Acid Orange 50	69	61
				2,5-Dichlorosulfanilic acid	0.6	--
				N-Ethyl-N-phenylbenzylamine	0.6	48
				By-products	0	39

---

[e] Probable main component made by nitration of C.I. 13080.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
ICI	13190	Reactive Yellow 4	>2.3	Reactive Yellow 4	69	61
				3-Amino-1,5-naphthalene disulfonic acid	0.4	--
				m-Toluidine	0.4	--
				Cyanuric chloride	--	48
				By-products	0	39
TRC	13245	Reactive Yellow 3	>2.3	Reactive Yellow 3	69	61
				3-Amino-1,5-naphthalene disulfonic acid	0.4	--
				N-(3-Aminophenyl) acetamide	0.4	--
				Cyanuric chloride	--	--
				Ammonia[f]	--	--
				By-products	0	39
PDC TRC	13250	Mordant Brown 33	>4.5	Mordant Brown 33	95	45
				2-Amino-4-nitrophenol	1.7	--
				2,4-Diaminobenzene sulfonic acid	1.7	140
				By-products	0	99

[f] Ammonia was not quantified but is assumed to be in the aqueous phase.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
PDC	13265	Mordant Brown 70	>2.3	Mordant Brown 70	48	23
				Picramic acid	0.9	--
				2,4-Diaminobenzene sulfonic acid	0.4	36
				N-(3-Amino-4-sulfophenyl) glycine	0.4	36
				By-products	0.	50
TRC	13361	Acid Green 35	>2.3	Acid Green 35	69	61
				Picramic acid	0.4	--
				Naphthionic acid	0.4	48.
				Chromium (Cr^{+3})	7.3	6.1
				By-products	0	39
ATL FAB	13390	Acid Blue 92	>9	Acid Blue 92	270	240
				H-Acid	2.2	--
				N-Phenyl Peri acid	2.2	190
				By-products	0	150

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
BAS GAF TRC	13900 13900:1	Acid Yellow 99 Solvent Yellow 19	>9.1	Acid yellow 99	270	250
				6-Amino-4-nitro-1-phenol-2-sulfonic acid	1.5	--
				Acetoacetanilide	1.5	190
				Chromium (Cr^{+3})	29	23
				By-products	0	150
AC DUP TRC VPC	13906	Acid Yellow 151	1620.9	Acid Yellow 151	48600	43800
				2-Amino-1-phenol-4-sulfonamide	270	--
				Acetoacetanilide	270	34000
				Cobalt (Cr^{+3})	5140	4380
				By-products	0	27600
ATL	13950	Direct Yellow 27	>2.3	Direct Yellow 27	69	61
				Dehydrothio-p-toluidine disulfonic acid	0.6	--
				o-Acetoacetanisidide	0.6	48
				By-products	0	39

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Wastewater
PDC	14025	Mordant Yellow 1	>2.3	Mordant Yellow 1	48	23
				m-Nitroaniline	0.8	--
				Salicylic acid	0.8	71
				By-products	0	50
PDC TRC	14030	Mordant Orange 1	>4.5	Mordant Orange 1	95	45
				p-Nitroaniline	1.7	--
				Salicylic acid	1.7	140
				By-products	0	99
PDC	14110	Mordant Yellow 20	>2.3	Mordant Yellow 20	48	23
				7-Amino-1,3-naphthalenedisulfonic acid	0.8	--
				Salicylic acid	0.8	71
				By-products	0	50

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Wastewater
TRC	14155	Direct Green 28	>2.3	Direct Green 28	69	61
				2-Amino-5-(4-amino-3-sulfo-1-anthraquinonylamino) benzene-sulfonic acid	0.3	--
				5-(p-Aminophenylazo)-salicylic acid	0.3	--
				Aniline	0.3	--
				Cyanuric chloride	--	--
				By-products	0	39
ATL TRC	14170	Acid Yellow 65	>4.5	Acid Yellow 65	138	120
				2-(p-Aminoanilino)-5-nitrobenzenesulfonic acid	0.8	--
				o-Cresol	0.8	--
				Benzenesulfonyl chloride	0.8	--
				By-products	0	78

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
BAS TRC	14645	Mordant Black 11	>45	Mordant Black 11	950	450
				1-Amino-6-nitro-2-naphthol-4-sulfonic acid	17	--
				1-Naphthol	17	1400
				By-products	0	990
ALT BCC	14700	Food Red 1	>4.5	Food Red 1	135	120
				5-Amino-2,4-Xylenesulfonic acid	1.1	--
				Nevile and Winther's acid	1.1	95
				By-products	0	77
AC BAS BDO GAF PDC TRC	14710	Acid Red 4	19.5	Acid Red 4	585	530
				o-Anisidine	4.9	--
				Nevile and Winther's acid	4.9	410
				By-products	0	330

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Wastewater
ATL	14720	Acid Red 14	>25.5	Acid Red 14	765	690
BAS		Food Red 3		Naphthionic acid	6.4	--
GAF		Mordant Blue 79		Nevile and Winther's acid	6.4	536
PDC						
				By-products	0	433
HSH	14830:1	Pigment Red 54	>0.5	Pigment Red 54	10	5
	14830	Acid Red 20		1-Naphthylamine	0.2	--
				1-Naphthol-5-sulfonic acid	0.2	15
				By-products	0	11
AC	14880	Acid Blue 158	>4.5	Acid Blue 158	140	120
TRC				1-Amino-2-naphthol-4-sulfonic acid	0.8	--
				1-Naphthol-8-sulfonic acid	0.8	95
				Chromium (Cr^{+3})	14	12
				By-products	0	76
AC	15050	Acid Blue 158:1	>4.5	Acid Blue 158:1	140	120
TRC				1-Amino-2-naphthol-4-sulfonic acid	0.8	--
				1-Naphthol-8-sulfonamide	0.8	95
				Chromium (Cr^{+3})	14	12
				By-products	0	76

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
AC	15510	Acid Orange 7	206.8	Acid Orange 7	6200	5580
ACY		Pigment Orange 17		Sulfanilic acid	52	--
ATL		Pigment Orange 17:1[g]		2-Naphthol	52	4340
BAS		Solvent Orange 49				
BDO				By-products	0	3520
GAF						
PDC						
TRC						
VPC						
AC	15575	Acid Orange 8	142.7	Acid Orange 8	4280	3840
ACY				4-Amino-m-toluene-sulfonic acid	36	--
ATL				2-Naphthol	36	3000
TRC						
VPC				By-products	0	2430
ACY IDC	15585	Pigment Red 53	1800	Pigment Red 53	37800	18000
AMS KON		D & C Red 8		2-Amino-5-chloro-p-toluene-sulfonic acid	675	--
APO MGR	15585:1	Pigment Red 53:1[g]				
BOR MRX		D & C Red 9		2-Naphthol	675	55800
CIK SDH						
HSC SNA				By-products	0	39600
HSH TMS						
ICC						

[g] :1 is the barium salt. No estimation of the release of this metal was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
BAS	15602	Pigment Orange 46	>0.5	Pigment Orange 46	10	5
				2-Amino-5-chloro-4-ethyl-benzenesulfonic acid	0.2	--
				2-Naphthol	0.2	15
				By-products	0	11
ATL BAS GAF TRC	15620	Acid Red 88	40	Acid Red 88	1200	1080
				Naphthionic acid	10	--
				2-Naphthol	10	840
				By-products	0	680
ACY ICC AMS IDC BNS KON BOR SDH CIK SNA HSC UHL	15630 15630:1 15630:2	Pigment Red 49 Pigment Red 49:1[h] Pigment Red 49:2[h]	3150	Pigment Red 49	66150	31500
				Tobias acid	1180	--
				2-Naphthol	1180	97650
				By-products	0	69300

[h] :1 is the barium salt, :2 is the calcium salt. No estimation of the release of these metals was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
PDC	15670	Mordant Violet 5	>2.3	Mordant Violet 5	48	23
				2-Amino-1-phenol-4-sulfonic acid	0.8	--
				2-Naphthol	0.8	71
				By-products	0	50
BAS TRC	15705	Mordant Black 17	>4.5	Mordant Black 17	95	45
				1-Amino-2-naphthol-4-sulfonic acid	1.7	--
				2-Naphthol	1.7	140
				By-products	0	99
AC SDH ATL BAS FAB TRC	15711	Acid Black 52	406.8	Acid Black 52	12200	1100
				1-Amino-6-nitro-2-naphthol-4-sulfonic acid	68	--
				2-Naphthol	68	8540
				Chromium (Cr^{+3})	1290	110
				By-products	0	6920

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
GLX HRC ICC ROM	15800:2	Pigment Brown 5	>1.8	Pigment Brown 5	38	18
				Aniline	0.7	--
				3-Hydroxy-2-naphthoic acid	0.7	56
				By-products	0	40
DUP HPC	15825	Pigment Red 58	>0.9	Pigment Red 58	19	9
				6-Chlorometanilic acid	0.4	--
				3-Hydroxy-2-naphthoic acid	0.4	28
				By-products	0	20
ACY AMS APO BNS BOR CIK DUP HPC HSH ICC IDC KON MGR SDH SNA TMS UHL	15850	Pigment Red 57	1550.0	Pigment Red 57	32550	15500
	15850:1	Pigment Red 57:1 [i]		6-Amino-m-toluene sulfonic acid	580	--
				3-Hydroxy-2-naphthoic acid	580	48000
				By-products	0	34100

[i] :1 is the calcium salt. No estimation of the release of this metal was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste-water
ACY MRX AMS SNA HPC UHL HSC HSH MGR	15860:1 15860:2	Pigment Red 52:1[j] Pigment Red 52:2[j]	798.6	Pigment Red 52	16770	7990
				2-Amino-5-chloro-p-toluenesulfonic acid	300	--
				3-Hydroxy-2-naphthoic acid	300	24700
				By-products	0	17600
ACY HSH AMS ICC BOR MGR DUP MRX HPC S HRC SNA HSC UHL	15865 15865:1-4	Pigment Red 48 Pigment Red 48:1-4[k]	1135.5	Pigment Red 48	23800	11400
				6-Amino-4-chloro-m-toluenesulfonic acid	426	--
				3-Hydroxy-2-naphthoic acid	426	35200
				By-products	0	25000
HSC HSH KON SNA	15880	Pigment Red 63	25.9	Pigment Red 63	544	259
				Tobias acid	9.7	--
				3-Hydroxy-2-naphthoic acid	9.7	803
				By-products	0	570

[j] :1 is the calcium salt, :2 is the manganese salt.

[k] :1 is the barium salt, :2 is the calcium salt, :3 is the strontium salt, :4 is the manganese salt. No estimation of the release of these metals was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
PSC	15970	Acid Orange 12 Food Orange 1	>2.3	Acid Orange 12	69	61
				Aniline	0.6	--
				Schaeffer's acid	0.6	48
				By-products	0	39
ALT BCC KON SDH STG WJ	15985	Food Yellow 3	488.2	Food Yellow 3	10300	4880
				Sulfanilic acid	183	--
				Schaeffer's acid	183	15134
				By-products	0	10700
ALT BCC KON SDH WJ	16035	Food Red 17	867.3	Food Red 17	18200	8670
				4-Amino-5-methoxy-o-toluene sulfonic acid	325	--
				Schaeffer's acid	325	26900
				By-products	0	19100

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste-water
SDH	16105	Mordant Red 9	>140.	Mordant Red 9	2940	1400
HSH	16105:1	Pigment Red 60:1[1]		Anthranilic acid	52	--
KON				R acid	52	4340
MRX						
SNA						
				By-products	0	3080
ACY	16150	Acid Red 26 Food Red 5	>2.3	Acid Red 26	69	61
				2,4-Xylidine	0.6	--
				R acid	0.6	48
				By-products	0	39
SDH	16185	Acid Red 27 Food Red 9	>2.3	Acid Red 27	69	61
				Naphthionic acid	0.6	--
				R acid	0.6	48
				By-products	0	39

[1] :1 is the barium salt. No estimation of the release of this metal was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC	16230	Acid Orange 10	65.9	Acid Orange 10	1980	1780
ACY		Food Orange 4		Aniline	16	--
ATL				G-acid	16	1380
BAS						
GAF						
TRC				By-products	0	1120
ATL	16255	Acid Red 18	>4.5	Acid Red 18	130	120
TRC		Food Red 7		Naphthionic acid	1.1	--
				G acid	1.1	94
				By-products	0	76
ACY	16580	Acid Violet 3	>6.8	Acid Violet 3	204	180
ATL				p-Nitroaniline	1.7	--
TRC						
				Chromotropic acid	1.7	140
				By-products	0	115

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste Water
BDO	17025	Acid Violet 1	>2.3	Acid Violet 1	69	61
				2-Amino-5-nitrobenzene-sulfonic acid	0.6	--
				Gamma acid	0.6	48
				By-products	0	39
AC IRC	17045	Acid Red 37	>4.5	Acid Red 37	135	120
				5-Acetamido-2-amino-benzene sulfonic acid	1.1	--
				Gamma acid	1.1	94
				By-products	0	76
ICI TRC	17053	Acid Red 57	>4.5	Acid Red 57	135	120
				2-Amino-N-ethyl-benzene-sulfonanilide	1.1	--
				Gamma acid	1.1	94
				By-products	0	76

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Wastewater
ACY	17100	Acid Brown 90	>2.3	Acid Brown 90	69	61
				p-Amino-α-toluene sulfonic acid	0.6	--
				Gamma acid	0.6	48
				By-products	0	39
BAS ALT ICI TRC	17101	Acid Red 266	>9.1	Acid Red 266	270	250
				4-Chloro-α,α,α-trifluoro-o-toluidine	2.3	--
				Gamma acid	2.3	190
				By-products	0	155
ATL ALT DUP TRC VPC	--	Acid Red 337	794	Acid Red 337	23800	21400
				α,α,α-Trifluoro-o-toluidine	200	--
				Gamma acid	200	16700
				By-products	0	13500
BCC KON	17200	Acid Red 33 Food Red 12	>4.5	Acid Red 33	135	120
				Aniline	1.1	--
				H-acid	1.1	94
				By-products	0	76

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
PDC	17590	Mordant Brown 40	>2.3	Mordant Brown 40	48	23
				Anthranilic acid	0.8	--
				N-Phenyl Gamma acid	0.8	71
				By-products	0	50
ATL BAS DUP GAF TRC VPC	17755	Acid Red 137	41.8	Acid Red 137	1250	1130
				p-Aminoacetanilide	10	--
				N-Acetyl J acid	10	878
				By-products	0	710
HST	17757	Reactive Orange 16	>2.3	Reactive Orange 16	69	61
				2-(p-Aminophenylsulfonyl) ethanol sulfate ester	0.6	--
				N-Acetyl Gamma acid	0.6	48
				By-products	0	39

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production Metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
ICI	17907	Reactive Orange 1	>2.3	Reactive Orange 1	69	61
				Orthanilic acid	0.4	--
				J Acid	0.4	--
				Cyanuric chloride	0	48
				By-products	0	39
ICI	17908	Reactive Red 8	>2.3	Reactive Red 8	69	61
				2-Amino-5-methoxy-benzene-sulfonic acid	0.4	--
				J acid	0.4	--
				Cyanuric chloride	--	48
				By-products	0	39
AC	18050	Acid Red 1	154.1	Acid Red 1	4620	4160
ACY		Food Red 10		Aniline	38	--
ATL				N-Acetyl H acid	38	3240
BDO						
DUP						
GAF						
TRC						
VPC				By-products	0	2620

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
ATL BDO	18055	Acid Violet 7 Food Red 11	>4.5	Acid Violet	135	120
				p-Aminoacetanilide	1.1	--
				N-Acetyl H acid	1.1	94
				By-products	0	76
BDO	18075	Acid Violet 12	>2.3	Acid Violet 12	69	61
				o-Anisidine	0.6	--
				N-Acetyl H acid	0.6	48
				By-products	0	39
HST	18097	Reactive Violet 5	>2.3	Reactive Violet 5	68	61
				2-(4-Amino-3-methoxyphenylsulfonyl) ethanol sulfate ester	0.4	--
				N-Acetyl H acid	0.4	48
				Copper (Cu^{+2})	7.3	6.1
				By-products	0	38

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production Metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
ICI	18158	Reactive Red 1	>2.3	Reactive Red 1	69	61
				2-Aminobenzenesulfonic acid	0.4	--
				H-Acid	0.4	--
				Cyanuric chloride	--	48
				By-products	0	39
TRC	18165	Acid Black 60	>2.3	Acid Black 60	69	61
				2-Amino-N-methyl-1-phenol-4-sulfonamide	0.4	--
				N-(7-Hydroxy-1-naphthyl) acetamide	0.4	48
				Chromium (Cr^{+3})	7.3	6.1
				By-products	0	39
FAB ICI	18200	Reactive Red 2	>4.5	Reactive Red 2	135	120
				Aniline	0.7	--
				H acid	0.7	--
				Cyanuric chloride	--	94
				By-products	0	76

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
FAB ICI	18260	Reactive Orange 4	>4.5	Reactive Orange 4	135	120
				2-Amino-1,5-naphthalene disulfonic acid	0.7	--
				N-Methyl J Acid	0.7	--
				Cyanuric chloride	--	94
				By-products	0	76
ICI	18270	Reactive Orange 13	>2.3	Reactive Orange 13	69	61
				2-Amino-1,5-naphthalene disulfonic acid	0.4	--
				N-Methyl-J acid	0.4	--
				Cyanuric chloride	--	--
				Ammonia[m]	--	--
				By-products	0	39

[m] Ammonia release was not quantified, but is assumed to be in the aqueous phase.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
BAS	18690	Acid Yellow 121 Solvent Yellow 21	>2.3	Acid Yellow 121	69	61
				Anthranilic acid	0.4	--
				3-Methyl-1-phenyl-5-pyrazolone	0.4	48
				Chromium (Cr^{+3})	7.3	6.1
				Formamide[n]	--	--
				By-products	0	39
AC ALT ATL DUP TRC VPC	18732	Acid Orange 60	298.6	Acid Orange 60	8960	8060
				2-Amino-1-phenol-4-sulfonamide	50	--
				3-Methyl-1-phenyl-5-pyrazolone	50	6270
				Chromium (Cr^{+3})	950	810
				By-products	0	5080
ACY	18740	Acid Orange 72	>2.3	Acid Orange 72	69	61
				2-Amino-6-nitro-1-phenol-4-sulfonic acid	0.4	--
				3-Methyl-1-phenyl-5-pyrazolone	0.4	48
				Chromium (Cr^{+3})	7.3	6.1
				By-products	0	39

[n] The dye is heated with chromium formate in formamide solution. No estimation of the quantity of this solvent was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste Water
GAF TRC	18745	Acid Orange 74	>4.5	Acid Orange 74	130	120
				Chromium (Cr^{+3})	13.8	12
				6-Amino-4-nitro-1-phenol-2-sulfonic acid	0.8	--
				3-Methyl-1-phenyl-5-pyrazolone	0.8	95
				By-products	0	77
ACY ATL BDO PDC	18760	Mordant Red 7	>9.1	Mordant Red 7	190	91
				1-Amino-2-naphthol-4-sulfonic acid	3.4	--
				3-Methyl-1-phenyl-5-pyrazolone	3.4	280
				By-products	0	200
AC	18810	Acid Red 186	>2.3	Acid Red 186	69	61
				1-Amino-2-naphthol-4-sulfonic acid	0.4	--
				3-Methyl-1-(m-sulfophenyl)-5-pyrazolone	0.4	48
				Chromium (Cr^{+3})	7.3	6.1
				By-products	0	39

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
BDO	18820	Acid Yellow 11	>2.3	Acid Yellow 11	69	61
				Aniline	0.6	--
				3-Methyl-1-(p-sulfophenyl)-5-pyrazolone	0.6	48
				By-products	0	39
PDC	18821	Mordant Yellow 8	>2.3	Mordant Yellow 8	48	23
				Anthranilic acid	0.8	--
				3-Methyl-1-(p-sulfophenyl)-5-pyrazolone	0.8	71
				By-products	0	50
AC	18835	Acid Yellow 25	>2.3	Acid Yellow 25	69	61
				5-Amino-o-toluenesulfonanilide	0.6	--
				3-Methyl-1-(p-sulfophenyl)-5-pyrazolone	0.6	48
				By-products	0	39

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
HST	18852	Reactive Yellow 17	>2.3	Reactive Yellow 17	69	61
				2-(4-Amino-3,6-dimethoxyphenylsulfonyl) ethanol sulfate ester	0.6	--
				3-Methyl-1-(4-sulfophenyl) -5-pyrazolone	0.6	48
				By-products	0	39
ATL BDO	18890	Acid Yellow 34	>4.5	Acid Yellow 34	135	120
				Aniline	1.1	--
				1-(2-Chloro-5-sulfophenyl)-3-methyl-5-pyrazolone	1.1	94
				By-products	0	76
TRC	18900	Acid Yellow 29	>2.3	Acid Yellow 29	69	61
				Metanilanilide	0.6	--
				1- (2-Chloro-5-sulfophenyl) -3-methyl-5-pyrazolone	0.6	48
				By-products	0	39

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste Water
DUP	18930	Acid Yellow 200	>2.3	Acid Yellow 200	69	61
				Tobias acid	0.6	--
				1-(2-Chloro-5-sulfophenyl) 3-methyl-5-pyrazolone	0.6	48
				By-products	0	39
ALT ATL TRC	18950	Acid Yellow 40	>6.8	Acid Yellow 40	204	180
				p-Aminophenol	1.1	--
				1-(4-Chloro-2-sulfophenyl) 3-methyl-5-pyrazolone	1.1	140
				p-Toluenesulfonyl chloride	1.1	140
				By-products	0	115
ATL BDO SDH TRC	18965	Acid Yellow 17 Food Yellow 5	84.1	Acid Yellow 17	2520	2270
				Sulfanilic acid	21	--
				1-(2,5-Dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone	21	1760
				By-products	0	1430

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC ALT ATL ICI	18967	Acid Yellow 19	>9.1	Acid Yellow 19	273	250
				Tobias acid	2.3	--
				1-(2,5-Dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone	2.3	190
				By-products	0	154
ICI	18971	Reactive Yellow 1	>2.3	Reactive Yellow 1	69	61
				2,4-Diaminobenzene sulfonic acid	0.4	--
				3-Methyl-1-(2,4-dichloro-4-sulfophenyl)-5-pyrazolone	0.4	48
				Cyanuric chloride	--	48
				By-products	0	39
TRC	18972	Reactive Yellow 2	>2.3	Reactive Yellow 2	69	61
				4-Aminobenzene sulfonic acid	0.3	48
				2,4-Diaminobenzene sulfonic acid	0.3	--
				3-Methyl-1-(2,4-dichloro-4-sulfophenyl)-5-pyrazolone	0.3	48
				Cyanuric chloride	--	48
				By-products	0	39

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
TRC	19005	Acid Yellow 127	>2.3	Acid Yellow 127	69	61
				2-Amino-4-(3-chloro-1-oxido-1,2,4-benzotriazine-7-carboxamido)benzene sulfonic acid	0.6	--
				1-(6-Chloro-o-tolyl)-3-methyl-5-pyrazolone	0.6	48
				By-products	0	39
AC TRC	19010	Acid Yellow 54	>4.5	Acid Yellow 54	140	120
				4-Sulfoanthranilic acid	0.8	--
				3-Methyl-1-(4-sulfo-o-tolyl)-5-pyrazolone	0.8	95
				Chromium salt	14	12
				By-products	0	77
ALT BCC KON SDH STG WJ AC ACY BAS GAF MRX TRC	19140	Acid Yellow 23 Food Yellow 4	730	Acid Yellow 23	21900	19700
				Sulfanilic acid	182	--
				3-Carboxy-1-(p-sulfophenyl) 5-pyrazolone	182	15300
				By-products	0	12400

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
TRC	19351	Acid Red 179	>2.3	Acid Red 179	69	61
				6-Amino-4-chloro-1-phenol-2-sulfonic acid	0.4	--
				2,4-Quinolinediol	0.4	48
				Chromium (Cr^{+3})	7.3	6.1
				By-products	0	39
ATL BAS DUP GAF PDC TRC	19555	Direct Yellow 28	25.9	Direct Yellow 28	780	700
				Sodium dihydrothio-p-toluidine sulfonate	13	--
				By-products	0	440

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
HST	20040	Pigment Yellow 16	>0.4	Pigment Yellow 16	9	4
				2,4 - Dichloroaniline	0.2	--
				4',4'''- Bi-o-acetoacetotoluidide	0.1	14
				By-products	0	28
ATL TRC	20110	Mordant Brown 1	>4.5	Mordant Brown 1	90	45
				2-Amino-4-nitrophenol	1.1	--
				5-Amino-1-naphthalenesulfonic acid	1.1	--
				m-Phenylenediamine	1.1	140
				By-products	0	280

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
PDC	20150	Mordant Brown 18	>2.3	Mordant Brown 18	46	23
				Sulfanilic acid	0.6	--
				p-Nitroaniline	0.6	--
				Salicylic acid	0.6	71
				By-products	0	142
ACY ATL BAS ALT FAB TRC	20170	Acid Orange 24	>13.6	Acid Orange 24	410	370
				Sulfanilic acid	2.3	--
				Xylidine (crude)	2.3	--
				Resorcinol	2.3	285
				By-products[a]	0	570
ACY	20177	Acid Brown 354	>2.3	Acid Brown 354	69	61
				2-(p-Aminoanilino)-5-nitrobenzenesulfonic acid	0.4	--
				Resorcinol	0.8	48
				By-products	0	96

[a] The by-product estimate assumed pure xylidine. Impurities in crude xylidine would increase the amount of by-products.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC ACY ATL BAS ALT TRC	20195	Acid Brown 14	106.4	Acid Brown 14	3190	2870
				Naphthionic acid	36	--
				Resorcinol	18	2230
				By-products	0	4470
VPC	20250	Acid Brown 83	>2.3	Acid Brown 83	69	61
				4-Methoxymetanilic acid	0.3	--
				Resorcinol	0.3	48
				4-Nitro-m-phenylenediamine	0.3	--
				Copper (Cu^{+2})	7.2	6.1
				Ammonia[p]	0	--
				By-products	0	96
PDC	20460	Acid Blue 29	>2.3	Acid Blue 29	69	61
				m-Nitroaniline	0.4	--
				Aniline	0.4	--
				H acid	0.4	48
				By-products	0	96

[p] Ammonia release was not quantified but is assumed to be in the aqueous phase.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC ALT ACY FAB ATL PDC BAS TRC BDO	20470	Acid Black 1	169.1	Acid Black 1	5070	4560
				p-Nitroaniline	28.2	--
				Aniline	28.2	--
				H acid	28.2	3550
				By-products	0	7100
PDC	20480	Acid Black 41	>2.3	Acid Black 41	69	61
				p-Nitroaniline	0.4	--
				Sulfanilic acid	0.4	--
				H acid	0.4	48
				By-products	0	96
ATL BDO PDC TRC	20495	Acid Green 20	>9.1	Acid Green 20	180	91
				p-Nitroaniline	2.3	--
				Aniline	2.3	--
				H acid	2.3	280
				By-products	0	560

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
HST	20505	Reactive Black 5	>2.3	Reactive Black 5	69	61
				2-(p-Aminophenylsulfonyl) ethanol sulfate ester	0.4	--
				H acid	0.8	48
				By-products	0	96
ACY DUP PSC TRC	21000	Basic Brown 1	41.8	Basic Brown 1	1250	1130
				m-Phenylenediamine	21	--
				By-products	0	1760
ACY BAS PSC TRC	21010 21010:1 21010:2	Basic Brown 4 Solvent Brown 12 Pigment Brown 3	>110	Basic Brown 4	3300	2970
				Toluene-2,4-diamine	55	--
				By-products	0	6890
BAS	21030	Basic Brown 2	>2.3	Basic Brown 2	69	61
				4-Methoxy-m-phenylenediamine	0.4	--
				m-Phenylenediamine	0.8	48
				By-products	0	96

[q] :2 is the phosphotungstomolybdic acid complex.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
BAS GAF	21230	Solvent Yellow 29	>4.5	Solvent Yellow 29	90	45
				4,4'-Cyclohexylidenedi-o-toluidine	1.1	--
				p-Cyclohexylphenol	2.2	140
				By-products	0	280
PSC	21240	Solvent Yellow 30	>2.3	Solvent Yellow 30	48	23
				4,4'-Benzylidenedi-2,5-xylidine	0.6	--
				p-Cresol	1.2	71
				By-products	0	142
BAS	21250	Solvent Red 22	>2.3	Solvent Red 22	48	23
				4,4'-(o-Chlorobenzylidene)-di-2,5-xylidine	0.6	--
				2-Naphthol	1.2	71
				By-products	0	142
TRC	24810	Acid Red 134	>2.3	Acid Red 134	69	61
				4,4'-Cyclohexylidenedi-o-anisidine	0.4	--
				4,6-Dihydroxy-2-naphthalenesulfonic acid	0.8	48
				By-products	0	96

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
ACY ATL BAS DUP LVR SDH TRC	24890	Direct Yellow 4	300.4	Direct Yellow 4	9010	8110
				4,4'-Diamino-2,2' stilbene-disulfonic acid	50	--
				Phenol	100	6310
				By-products	0	12600
ACY ATL TRC	24895	Direct Yellow 12	>6.8	Direct Yellow 12	200	180
				4,4'-Diamino-2,2' stilbene-disulfonic acid	1.1	--
				Phenol	2.2	--
				Ethyl chloride	0	--
				By-products	0	285
ATL	25100	Mordant Yellow 16	>2.3	Mordant Yellow 16	46	23
				4,4'(and 2,4')-Thiodianiline	0.6	--
				Salicylic acid	1.2	71
				By-products	0	140

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
ATL	25135	Acid Yellow 38	>2.3	Acid Yellow 38	69	61
				6,6' Thiodimetanilic acid	0.4	--
				Phenol (2 mol)	0.8	--
				Ethyl chloride	0	--
				By-products	0	95
TRC	25200	Direct Orange 73	>2.3	Direct Orange 73	69	61
				3,3'-Diaminobenzanilide	0.4	--
				3-Carboxy-1-(m-nitrophenyl)-5-pyrazolone (2 mol)	0.8	--
				By-products	0	95
ATL	25380	Direct Red 75	>2.3	Direct Red 75	60	61
				5,5'-Ureylenebis(2-aminobenzene)sulfonic acid	0.4	--
				Gamma acid	0.8	47
				Phosgene[r]	--	--
				By-products	0	95

[r] Phosgene is assumed to be unstable.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste Water
MRT	26050	Solvent Red 19	>2.3	Solvent Red 19	48	23
				p-Phenylazoaniline	0.8	--
				N-Ethyl-2-naphthylamine	0.8	71
				By-products	0	142
ATL ALT EKT TRC	26070	Disperse Yellow 23	217.7	Disperse Yellow 23	4350	2180
				p-Phenylazoaniline	82	--
				Phenol	82	6750
				By-products	0	142
AC ALT BAS SDC VPC	26077	Disperse Orange 29	196.8	Disperse Orange 29	3940	1970
				p-Nitroaniline	49	--
				o-Anisidine	49	--
				Phenol	49	6100
				By-products	0	12200

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
PSC	26100	Solvent Red 23	>2.3	Solvent Red 23	48	23
				p-Phenylazoaniline	0.8	--
				2-Naphthol	0.8	71
				By-products	0	140
AC ACY ATL PSC	26105	Solvent Red 24	>9.1	Solvent Red 24	182	91
				4-o-Tolylazo-o-toluidine	3.4	--
				2-Naphthol	3.4	280
				By-products	0	560
ACY PSC	26120	Solvent Red 26	>4.5	Solvent Red 26	90	45
				o-Toluidine	1.1	--
				2,5-Xylidine	1.1	--
				2-Naphthol	1.1	140
				By-products	0	280

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
PSC	26125	Solvent Red 27	>2.3	Solvent Red 27	48	23
				Xylylazoxylidine	0.8	--
				2-Naphthol	0.8	71
				By-products	0	14
AC ALT	26360	Acid Blue 113	>9	Acid Blue 113	270	240
				Metanilic acid	1.5	--
				1-Naphthylamine	1.5	--
				N-Phenyl Peri acid	1.5	190
				By-products	0	380
AC	26370	Acid Black 24	>2.3	Acid Black 24	69	61
				5-Amino-1-naphthalenesulfonic acid	0.4	--
				1-Naphthylamine	0.4	--
				N-Phenyl Peri acid	0.4	48
				By-products	0	96

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC	26410	Acid Blue 118	>2.3	Acid Blue 118	69	61
				Aniline	0.4	--
				1,7-Cleve's Acid	0.4	--
				N-p-Tolyl Peri acid	0.4	48
				By-products	0	96
ICI	26440	Reactive Brown 1	>2.3	Reactive Brown 1	69	61
				Sulfanilic acid	0.2	--
				o-Aminobenzenesulfonic acid	0.2	--
				1,6(and 1,7)-Cleve's acid	0.2	--
				Cyanuric chloride	0	--
				By-products	0	96
ATL BAS PDC TRC	26520	Mordant Orange 6	>9.1	Mordant Orange 6	180	91
				p-(p-Aminophenylazo)benzenesulfonic acid	3.4	--
				Salicylic acid	3.4	280
				By-products	0	560

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
TRC	26550	Acid Orange 51	>2.3	Acid Orange 51	69	61
				2-(p-Aminoanilino)-5-nitrobenzenesulfonic acid	0.3	--
				1,6(and 1,7)-Cleve's acid	0.3	--
				o-Cresol	0.3	--
				p-Toluenesulfonyl chloride	0.3	--
				By-products	0	96
AC ACY ATL ALT DUP TRC VPC	26900	Acid Red 151	>15.9	Acid Red 151	477	430
				p-(p-Aminophenylazo)benzenesulfonic acid	4	--
				2-Naphthol	4	330
				By-products	0	660
AC	26905	Acid Red 66	>2.3	Acid Red 66	69	61
				6-Amino-3,4'-azodibenzenesulfonic acid	0.6	--
				2-Naphthol	0.6	48
				By-products	0	96

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
ATL	27200	Acid Red 115	>4.5	Acid Red 115	135	120
				4-o-Tolylazo-o-toluidine	1.1	--
				R acid	1.1	94
				By-products	0	190
ACY ATL BAS ALT PSC TRC	27290	Acid Red 73	74.5	Acid Red 73	2240	2010
				p-Phenylazoaniline	18	--
				G acid	18	1560
				By-products	0	3130
PSC	27291	Solvent Red 30	>2.3	Solvent Red 30[s]	48	23
				p-Phenylazoaniline	0.6	--
				G Acid	0.6	71
				Dicyclohexylamine[s]	0.6	71
				By-products	0	97
ATL TRC	27680	Direct Red 16	>4.5	Direct Red 16	135	120
				Aniline	0.7	--
				J acid	1.4	94
				By-products	0	190

[s] Convert C.I. 27290 to the dicyclohexylamine salt.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
ATL	27855	Direct Violet 7	>2.3	Direct Violet 7	69	61
				2-Amino-3,5-xylenesulfonic acid	0.4	--
				2,5-Xylidine	0.4	--
				N-Phenyl J acid	0.4	48
				By-products	0	96
ATL TRC	27885	Direct Violet 9	>4.5	Direct Violet 9	135	120
				Sulfanilic acid	0.7	--
				Cresidine	0.7	--
				N-Phenyl J acid	0.7	94
				By-products	0	190
ATL	27925	Direct Blue 67	>2.3	Direct Blue 67	69	61
				Cresidine	0.4	--
				N-Phenyl J acid	0.4	48
				H acid	0.4	--
				By-products	0	96

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC ACY ATL BAS ALT DUP LVR TRC	28160	Direct Red 81	1066.4	Direct Red 81	32000	28800
				p-(p-Aminobenzylazo) benzene sulfonic acid	266	--
				N-Benzoyl J acid	266	22400
				By-products	0	44800
DUP	28255	Direct Orange 74	>4.5	Direct Orange 74	135	120
				7-Amino-3-naphthalene-disulfonic acid	0.8	--
				m-Toluidine	0.8	--
				p-Nitrobenzoyl chloride	0.8	--
				N-p-Aminobenzoyl J acid	0.8	140
				By-products	0	285
AC ALT TRC	29000	Direct Yellow 44	>6.8	Direct Yellow 44	200	180
				Metanilic acid	0.8	--
				o-Anisidine	0.8	140
				p-Nitroaniline	0.8	--
				Salicylic acid	0.8	140
				Phosgene[t]	--	--
				By-products	0	285

---

[t] Phosgene is assumed to be unstable.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC ALT FAB TRC	29025	Direct Yellow 50	102.3	Direct Yellow 50	3070	2760
				3-Amino-1,5-naphthalene disulfonic acid	26	--
				m-Toluidine	26	2150
				Phosgene[t]	--	--
				By-products	0	4300
FAB	29030	Direct Yellow 51	>2.3	Direct Yellow 51	69	61
				3-Amino-1,5-naphthalene disulfonic acid	0.6	--
				2,5-Xylidine	0.6	48
				Phosgene[t]	--	--
				By-products	0	96
TRC	29042	Direct Yellow 118	>2.3	Direct Yellow 118	69	61
				Metanilic acid	0.3	--
				o-Anisidinomethane sulfonic acid	0.3	48
				7-Amino-1,3-naphthalene disulfonic acid	0.3	--
				m-Toluidine	0.3	48
				Phosgene[t]	--	--
				By-products	0	96

[t] Phosgene is assumed to be unstable.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
AC FAB TRC	29058	Direct Orange 72	>6.8	Direct Orange 72	204	180
				7-Amino-1,3-naphthalene-disulfonic acid	1.7	--
				Cresidine	1.7	140
				Phosgene[t]	--	--
				By-products	0	285
AC ALT TRC	29060	Direct Yellow 34	>6.8	Direct Yellow 34	204	180
				3-Amino-1,5-naphthalene-disulfonic acid	1.7	--
				Cresidine	1.7	140
				Phosgene[t]	--	--
				By-products	0	285
ALT TRC	29065	Direct Red 79	>4.5	Direct Red 79	135	121
				o-p-Tolylsulfonyl H acid	1.1	--
				Cresidine	1.1	94
				Phosgene[t]	--	--
				By-products	0	190

[t] Phosgene is assumed to be unstable.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
ATL TRC	29100	Direct Red 31	>4.5	Direct Red 31	135	120
				Aniline (2 mol)	1.4	--
				6,6'-Iminobis-1-naphthol-3-sulfonic acid	0.7	94
				By-products	0	190
ATL	29105	Direct Violet 14	>2.3	Direct Violet 14	69	61
				2,4-Xylidine (2 mol)	0.8	--
				6,6'-Iminobis-1-naphthol-3-sulfonic acid	0.4	48
				By-products	0	96
ATL	29110	Direct Red 149	>2.3	Direct Red 149	69	61
				m-Aminoformanilide (2-mol)	0.8	--
				6,6'-Iminobis-1- naphthol-3-sulfonic acid	0.4	48
				By-products	0	96

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste Water
ATL TRC	29120	Direct Violet 66	>4.5	Direct Violet 66	135	120
				2-Amino-1-phenol-4-sulfonamide	0.7	--
				6,6'-Iminobis-1-naphthol-3-sulfonic acid	0.7	94
				Copper (Cu^{+2})	14	12
				By-products	0	190
TRC	29155	Direct Orange 29	>2.3	Direct Orange 29	69	61
				Aniline	0.4	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	0.4	48
				m-Aminobenzoic acid	0.4	--
				By-products	0	96
AC ACY ATL BAS DVP	29156	Direct Orange 102	192.3	Direct Orange 102	5770	5190
				Aniline	32	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	32	4040
				p-Aminobenzoic acid	32	--
				By-products	0	8070

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr)	
					Solid Residue	Waste water
AC ACY ATL ALT DUP FAB TRC	29160	Direct Red 23	65.4	Direct Red 23	1960	1770
				Aniline	10.9	--
				6,6' Ureylenebis-1-naphthol-3-sulfonic acid	10.9	1370
				p-Aminoacetanilide	10.9	--
				By-products	0	2750
TRC	29165	Direct Red 4	>2.3	Direct Red 4	69	61
				Aniline	0.4	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	0.4	48
				Broenner's acid	0.4	--
				By-products	0	96
ATL TRC	29175	Direct Red 62	>4.5	Direct Red 62	135	120
				o-Toluidine	0.7	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	0.7	94
				4-Amino-m-toluenesulfonic acid (buffered with acetic acid)[u]	0.7	--
				By-products	0	190

[u] Acetic acid release was not quantified but is assumed to be in the aqueous phase.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC	29180	Direct Red 73	>2.3	Direct Red 73	69	61
				o-Toluidine	0.4	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	0.4	48
				Broenner's acid	0.4	--
				By-products	0	96
AC ATL ALT FAB TRC	29185	Direct Red 24	94.1	Direct Red 24	2820	2540
				4-Amino-m-toluenesulfonic acid	16	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	16	1980
				o-Anisidine	16	--
				By-products	0	3950
ATL	29190	Direct Red 26	>2.3	Direct Red 26	69	61
				o-Anisidine	0.4	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	0.4	48
				Naphthionic acid	0.4	--
				By-products	0	96

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
ATL BAS ALT DUP TRC	29200	Direct Red 72	266.4	Direct Red 72	7990	7190
				o-Anisidine (0.6 mol)	27	--
				o-Toluidine (0.4 mol)	17	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	44	5590
				Broenner's acid	44	--
				By-products	0	11200
TRC	29210	Direct Red 122	>2.3	Direct Red 122	69	61
				m-Aminoformanilide (2 mol)	0.8	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	0.4	48
				By-products	0	96
AC ATL ALT FAB TRC	29225	Direct Red 83	67.3	Direct Red 83	2000	1800
				4-Methoxymetanilic acid (2 mol)	16	--
				6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	8	1400
				Copper (Cu^{+2})	210	180
				Ammonia[v]	0	--
				By-products	0	2800

[v] Ammonia release was not quantified but is assumed to be in the aqueous phase.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC	30015	Direct Black 78	>2.3	Direct Black 78	69	61
				1,6(and 1,7)-Cleve's acid	0.3	48
				p-Nitroaniline	0.6	--
				S acid	0.3	48
				By-products	0	180
AC ATL ALT FAB	31600	Direct Black 80	>9.5	Direct Black 80	285	255
				Gamma Acid	2.4	200
				1,6(and 1,7)-Cleve's acid	1.2	200
				p-Aminoacetanilide	1.2	--
				By-products	0	730
ATL	34010	Direct Blue 126	>2.3	Direct Blue 126	69	61
				3-Amino-1,5-naphthalene disulfonic acid	0.3	--
				1-Naphthylamine	0.3	--
				1,6(and 1,7)-Cleve's acid	0.3	--
				Cresidine	0.3	48
				By-products	0	180

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
TRC	34045	Direct Green 26	>2.3	Direct Green 26	69	61
				Cyanuric Chloride	--	--
				H acid	0.2	--
				p-Nitroaniline	0.2	--
				Salicylic acid	0.2	--
				Aniline	0.2	--
				Cresidine	0.2	--
				By-products	0	180
AC TRC	34085	Direct Blue 120	>4.5	Direct Blue 120	135	120
				p-Aminooxanilic acid	0.6	--
				1,6-Cleve's acid	1.2	--
				Nevile and Winther's acid	0.6	94
				By-products	0	340
AC TRC	34090	Direct Blue 120A	>4.5	Direct Blue 120A	135	120
				p-Aminooxanilic acid	0.6	--
				1,6-Cleve's acid	1.2	--
				Schaeffer's acid	0.6	94
				By-products	0	340

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production Metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Waste water
AC	34200	Direct Blue 78	>2.3	Direct Blue 78	69	61
				2-Amino-p-benzene-disulfonic acid	0.3	--
				1,7-Cleve's acid	0.3	--
				1-Naphthylamine	0.3	--
				N-Phenyl J acid	0.3	48
				By-products	0	180
TRC	34220	Direct Blue 75	>2.3	Direct Blue 75	69	61
				Metanilic acid	0.3	--
				1,6-Cleve's acid	0.6	--
				N-Phenyl J acid	0.3	48
				By-products	0	180
TRC	34260	Direct Green 51	>2.3	Direct Green 51	69	61
				Metanilic acid	0.3	--
				1,7-Cleve's acid	0.3	--
				5-Amino-6-ethoxy-2-naphthalene sulfonic acid	0.3	--
				N-m-Aminobenzoyl J acid	0.3	48
				Pyridine[w]	--	--
				By-products	0	180

[w] Pyridine is used as a solvent. No estimation of the quantity of this solvent was made.

Table 12 (Continued)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Waste water
FAB	35005	Direct Brown 44	>4.5	Direct Brown 44	136	123
				Sulfanilic acid	0.9	--
				m-Phenylenediamine	1.4	96
				By-products	0	690
TRC	35255	Direct Black 19	>2.3	Direct Black 19	69	61
				p-Nitroaniline	0.5	--
				m-Phenylenediamine	0.5	48
				H acid	0.2	--
				By-products	0	350
AC ATL ALT TRC VPC	35435	Direct Black 22	>11.4	Direct Black 22	342	308
				5-Amino-2-(p-aminoanilino)-benzenesulfonic acid	1.2	--
				Gamma Acid	2.4	--
				m-Phenylenediamine	2.4	239
				By-products	0	1740

Table 12 (Concluded)

Producer	C.I. No.	Dye	Annual Production metric tons/yr	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Waste water
AC ATL ALT FAB TRC	35780	Direct Red 80	200.9	Direct Red 80	6030	5420
				6-Amino-3,4'-azodibenzene-sulfonic acid	50	--
				N-Acetyl J acid	50	--
				Phosgene[x]	--	--
				By-products	0	30500

[x] Phosgene is assumed to be unstable.

Table 13

INTERMEDIATES USED IN TABLE 12 THAT HAVE COMMON NAMES

1-Amino-4-naphthalene sulfonic acid	(Naphthionic acid)
1-Amino-6-naphthalene sulfonic acid	(1,6-Cleve's acid)
1-Amino-7-naphthalene sulfonic acid	(1,7-Cleve's acid)
2-Amino-6-naphthalene sulfonic acid	(Broenner's acid)
1-Amino-8-hydroxy-4-naphthalene sulfonic acid	(S acid)
6-Amino-4-hydroxy-2-naphthalene sulfonic acid	(Gamma acid)
7-Amino-4-hydroxy-2-naphthalene sulfonic acid	(J acid)
1-Amino-8-hydroxy-3,6-naphthalene disulfonic acid	(H acid)
4-Amino-5-hydroxy-1,3-naphthalene disulfonic acid	(Chicago acid)
1,8-Dihydroxy-3,6-naphthalene disulfonic acid	(Chromotrophic acid)
2-Hydroxy-3,6-naphthalene disulfonic acid	(R acid)
2-Hydroxy-6,8-naphthalene disulfonic acid	(G acid)
N-Acetyl-1-amino-8-hydroxy-3,6-naphthalene disulfonic acid	(N-Acetyl H acid)
N-Acetyl-2-amino-5-hydroxy-7-naphthalene sulfonic acid	(N-Acetyl J acid)
N-Acetyl-7-amino-1-hydroxy-3-naphthalene sulfonic acid	(N-Acetyl Gamma acid)
N-Benzoyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	(N-Benzoyl J acid)
N-Phenyl-1-amino-8-naphthalene sulfonic acid	(N-Phenyl Peri acid)
N-Phenyl-2-amino-8-hydroxy-6-naphthalene sulfonic acid	(N-Phenyl Gamma acid)
N-Phenyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	(N-Phenyl J acid)

Table 13 (Concluded)

N-m-Aminobenzoyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	(N-m-Aminobenzoyl J acid)
N-p-Aminobenzoyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	(N-p-Aminobenzoyl J acid)
N-p-Tolyl-1-amino-8-naphthalene sulfonic acid	(N-p-Tolyl Peri acid)
o-Phenylsulfonyl-1-amino-8-hydroxy-3,6-naphthalene disulfonic acid	(o-Phenylsulfonyl H acid)
o-Phenylsulfonyl-2-amino-8-hydroxy-3,6-naphthalene disulfonic acid	(o-Phenylsulfonyl 2 R acid)
o-Tolysulfonyl-1-amino-8-hydroxy-3,6-naphthalene disulfonic acid	(o-Tolylsulfonyl H acid)
2-Aminobenzene sulfonic acid	(Orthanilic acid)
4-Aminobenzene sulfonic acid	(Sulfanilic acid)
3-Methyl-2-hydroxy-benzoic acid	(2,3-Cresotic acid)

Table 14

DIRECTORY OF AZO DYE AND ORGANIC PIGMENT MANUFACTURERS, 1978

Names of manufacturers that reported production and/or sales of azo dyes and pigments (other than those based on benzidine and its congeners) to the U.S. International Trade Commission for 1978 are listed below in order of their identification codes as used in Table 12.

Code	Name of Company
AC	American Color ¢ Chemical Corp.
ACY	American Cyanamid Co.
ALL	Alliance Chemical Corp.
ALT	Crompton & Knowles Corp., Dyes and Chemical Div.
AMS	Ridgway Color & Chemicals
APO	Apollo Colors, Inc.
ATL	Atlantic Chemical Corp.
BAS	BASF Wyandotte Corp.
BCC	Buffalo Color Corp.
BDO	Benzenoid Organics Inc.
BNS	Binney and Smith, Inc.
BOR	Borden, Inc., Printing Ink Div., Pigments Div.
BUC	Synalloy Corp., Blackman-Uhler Chemical Div.
CGY	Ciba-Geigy Corp.
CIK	Flint Ink Corp.
DUP[a]	E.I. du Pont de Nemours & Co., Inc.
EKT	Eastman Kodak Co.
FAB	Fabricolor Incorporated
GAF[b]	GAF Corp.
GLX	Galaxie Chemical Corp.
HPC	Hercules, Inc.
HRC	Harmon Colors Corp.
HSC[c]	Chemetron Corp., Pigments Div., Subsid. of Allegheny Ludlum Industries, Inc.
HST	American Hoechst Corp.
ICC	Inmont Corp.
ICI	ICI Americas Inc.
IDC	Industrial Color, Inc.
IND	Indol Chemical Co., Inc.
KWC	Keystone Color Works Inc.
KON	H. Kohnstamm & Co., Inc.
LVR	C. Lever Co. Inc.
MAY	Otto B. May Co. Div. of Cone Mills Corp.
MGR	Magruder Color Co.
MRT	Morton Norwich Products Inc.
MRX	Max Marx Color & Chem. Co.
PCW	Pfister Chemical Works
PDC	Berncolors-Poughkeepsie Co.
PSC	Passaic Color & Chem. Co.
ROM	United Merchants & Manufacturers, Inc. Roma Chemical Div.
S	Sandoz, Inc., Colors & Chemicals Div.
SDC	Martin-Marietta Corp.
SDH	Sterling Drug, Inc. Hilton Davis Chemical Co. Div.
SNA	Sun Chemical Corp., Pigments Div.
STG	Stange Co.
TMS	Sterling Drug, Inc., Thomasset Colors Div.

Table 14 (Concluded)

HSH	Harshaw Chemical Co.
TRC	Toms River Chemical Corp.
UHL	Paul Uhlich & Co. Inc.
VPC	Mobay Chemical Corp. Verona Dyestuff Div.
WJ	Warner-Jenkinson Co.

---

[a] In 1979 duPont sold its paper dye operations to Mobay Chemical Corp., and its textile dye operations to Ciba-Geigy Corp. and Crompton and Knowles Corp. In 1979 duPont sold its dyes for ink operations to Morton Norwich Products Inc., Morton Chemical Co. Division.

[b] In 1978 GAF Corp. sold its dye operations to BASF Wyandotte Corp.

[c] In 1978 Chemetron Corp. sold its dye operations to BASF Wyandotte Corp.

Table 15

PRODUCERS OF MONOAZO DYES AND PIGMENTS

C.I. No.	C.I. Name
American Color & Chemical Corp.	
18967	Acid Yellow 19
18835	Acid Yellow 25
19010	Acid Yellow 54
13906	Acid Yellow 151
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
15575	Acid Orange 8
16230	Acid Orange 10
13150	Acid Orange 50
18732	Acid Orange 60
18050	Acid Red 1
14710	Acid Red 4
17045	Acid Red 37
18810	Acid Red 186
14880	Acid Blue 158
15711	Acid Black 52
19140	Food Yellow 4
19140:1	Pigment Yellow 100
11855	Disperse Yellow 3
11005	Disperse Orange 3
11110	Disperse Red 1
11215	Disperse Red 5
11150	Disperse Red 7
11210	Disperse Red 17
11228	Disperse Red 65
11152	Disperse Brown 1
11365	Disperse Black 1
15050	Acid Blue 158:1
13095	Acid Yellow 63
13091	Acid Orange 1
American Cyanamid Co.	
13080	Acid Orange 5
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
15575	Acid Orange 8
16230	Acid Orange 10
18740	Acid Orange 72
18050	Acid Red 1
16150	Acid Red 26
16580	Acid Violet 3
19140	Food Yellow 4
19140:1	Pigment Yellow 100
12055	Solvent Yellow 14
11021	Solvent Yellow 56
12140	Solvent Orange 7
11320	Basic Orange 1
11320:1	Solvent Orange 4
11270	Basic Orange 2
11270:1	Solvent Orange 3
11052	Basic Blue 54
18760	Mordant Red 7
12075	Pigment Orange 5
12120	Pigment Red 3
12085	Pigment Red 4
12390	Pigment Red 17
12315	Pigment Red 22

Table 15 (Continued)

C.I. No.	C.I. Name
12355	Pigment Red 23
15865	Pigment Red 48
15630	Pigment Red 49
15860	Pigment Red 52
15585	Pigment Red 53
15850	Pigment Red 57
17100	Acid Brown 90
11043	Basic Violet 18
11014	Basic Red 30
11480	Basic Yellow 24
Crompton & Knowles Corp., Dyes and Chemical Div.	
17101	Acid Red 266
18967	Acid Yellow 19
18732	Acid Orange 60
15985	Food Yellow 3
19140	Food Yellow 4
19140:1	Pigment Yellow 100
11855	Disperse Yellow 3
11005	Disperse Orange 3
11227	Disperse Orange 25
11110	Disperse Red 1
11215	Disperse Red 5
11210	Disperse Red 17
11228	Disperse Red 65
11152	Disperse Brown 1
14700	Food Red 1
16035	Food Red 17
18950	Acid Yellow 40
—	Acid Red 337
—	Disperse Blue 79
Ridgway Color & Chemicals	
11680	Pigment Yellow 1
12085	Pigment Red 4
15865	Pigment Red 48
15630	Pigment Red 49
15860	Pigment Red 52
15585	Pigment Red 53
15850	Pigment Red 57
Apollo Colors, Inc.	
15585	Pigment Red 53
15850	Pigment Red 57
Atlantic Chemical Corp.	
18965	Acid Yellow 17
18967	Acid Yellow 19
18890	Acid Yellow 34
14170	Acid Yellow 65
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
15575	Acid Orange 8
16230	Acid Orange 10
13025	Acid Orange 52
18732	Acid Orange 60
18050	Acid Red 1
14720	Acid Red 14
16255	Acid Red 18
15620	Acid Red 88
17755	Acid Red 137
16580	Acid Violet 3
18055	Acid Violet 7
13390	Acid Blue 92
15711	Acid Black 52
12055	Solvent Yellow 14
12140	Solvent Orange 7
11270	Basic Orange 2
11270:1	Solvent Orange 3

Table 15 (Continued)

C.I. No.	C.I. Name
11085	Basic Red 18
13950	Direct Yellow 27
18760	Mordant Red 7
19555	Direct Yellow 28
11005	Disperse Orange 3
11100	Disperse Orange 5
11119	Disperse Orange 30
11110	Disperse Red 1
11115	Disperse Red 13
11152	Disperse Brown 1
18950	Acid Yellow 40

BASF Wyandotte Corp.

13065	Acid Yellow 36
13900	Acid Yellow 99
13900:1	Solvent Yellow 19
18690	Acid Yellow 121
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
16230	Acid Orange 10
14710	Acid Red 4
14720	Acid Red 14
15620	Acid Red 88
17101	Acid Red 266
17755	Acid Red 137
15711	Acid Black 52
19140	Food Yellow 4
19140:1	Pigment Yellow 100
12715	Solvent Red 8
11270	Basic Orange 2
11270:1	Solvent Orange 3
—	Acid Red 337
—	Disperse Blue 79

C.I. No.	C.I. Name
11085	Basic Red 18
11460	Basic Red 29
11154	Basic Blue 41
11052	Basic Blue 54
15602	Pigment Orange 46
19555	Direct Yellow 28
14645	Mordant Black 11
15705	Mordant Black 17
11110	Disperse Red 1
11115	Disperse Red 13
11210	Disperse Red 17
11116	Disperse Red 73
11480	Basic Yellow 24

Buffalo Color Corporation

17200	Acid Red 33
15985	Food Yellow 3
19140	Food Yellow 4
19140:1	Pigment Yellow 100
12156	Solvent Red 80
14700	Food Red 1
16035	Food Red 17

Benzenoid Organics Inc.

18820	Acid Yellow 11
18965	Acid Yellow 17
18890	Acid Yellow 34
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
18050	Acid Red 1
14710	Acid Red 4
17025	Acid Violet 1

Table 15 (Continued)

C.I. No.	C.I. Name
18055	Acid Violet 7
18075	Acid Violet 12
18760	Mordant Red 7
Binney and Smith, Inc.	
11710	Pigment Yellow 3
12390	Pigment Red 17
12300	Pigment Red 21
15630	Pigment Red 49
15850	Pigment Red 57
Borden, Inc., Printing Ink Div., Pigments Div.	
15865	Pigment Red 48
15630	Pigment Red 49
15585	Pigment Red 53
15850	Pigment Red 57
Synalloy Corp., Blackman-Uhler Chemical Div.	
12355	Pigment Red 23
11152	Disperse Brown 1
Ciba-Geigy Corp.	
12070	Pigment Red 1
Flint Ink Corp.	
12120	Pigment Red 3
15630	Pigment Red 49
15585	Pigment Red 53
15850	Pigment Red 57
E. I. du Pont de Nemours & Co., Inc.	
13065	Acid Yellow 36
13906	Acid Yellow 151
18930	Acid Yellow 200
18732	Acid Orange 60
18050	Acid Red 1
17755	Acid Red 137
12055	Solvent Yellow 14
11270	Basic Orange 2
11270:1	Solvent Orange 3
11056	Basic Orange 24
11085	Basic Red 18
11680	Pigment Yellow 1
11741	Pigment Yellow 74
12120	Pigment Red 3
12090	Pigment Red 6
12315	Pigment Red 22
12355	Pigment Red 23
15865	Pigment Red 48
15850	Pigment Red 57
15825	Pigment Red 58
12775	Pigment Green 10
19555	Direct Yellow 28
11227	Disperse Orange 25
11110	Disperse Red 1
12476	Disperse Red 220
11077	Disperse Blue 165
11087	Basic Yellow 15
	Acid Red 337
Eastman Kodak Co.	
11855	Disperse Yellow 3
11100	Disperse Orange 5
11227	Disperse Orange 25
11110	Disperse Red 1
11210	Disperse Red 17
11228	Disperse Red 65
	Disperse Blue 79
Fabricolor Incorporated	
13390	Acid Blue 92

Table 15 (Continued)

C.I. No.	C.I. Name
15711	Acid Black 52
11119	Disperse Orange 30
18200	Reactive Red 2
18260	Reative Orange 4
—	Disperse Red 54
GAF Corp.	
13900	Acid Yellow 99
13900:1	Solvent Yellow 19
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
16230	Acid Orange 10
18745	Acid Orange 74
18050	Acid Red 1
14710	Acid Red 4
14720	Acid Red 14
15620	Acid Red 88
17755	Acid Red 137
19140	Food Yellow 4
19140:1	Pigment Yellow 100
11320	Basic Orange 1
11320:1	Solvent Orange 4
11270	Basic Orange 2
11270:1	Solvent Orange 3
11085	Basic Red 18
11052	Basic Blue 54
12490	Pigment Red 5
19555	Direct Yellow 28
11110	Disperse Red 1
11115	Disperse Red 13
11210	Disperse Red 17

C.I. No.	C.I. Name
Galaxie Chemical Corp.	
11680	Pigment Yellow 1
11741	Pigment Yellow 74
12490	Pigment Red 5
12315	Pigment Red 22
12355	Pigment Red 23
12320	Pigment Red 32
15800:2	Pigment Brown 5
15800	Pigment Red 64
Hercules, Inc.	
11680	Pigment Yellow 1
11710	Pigment Yellow 3
11660	Pigment Yellow 5
11670	Pigment Yellow 6
11738	Pigment Yellow 73
11741	Pigment Yellow 74
11770	Pigment Yellow 75
12060	Pigment Orange 2
12075	Pigment Orange 5
12310	Pigment Red 2
12120	Pigment Red 3
12085	Pigment Red 4
12490	Pigment Red 5
12460	Pigment Red 9
12395	Pigment Red 13
12390	Pigment Red 17
12315	Pigment Red 22
12355	Pigment Red 23
15865	Pigment Red 48
15860	Pigment Red 52
15850	Pigment Red 57
15825	Pigment Red 58
12370	Pigment Red 112
12775	Pigment Green 10

Table 15 (Continued)

C.I. No.	C.I. Name
Harmon Colors Corp.	
11680	Pigment Yellow 1
11710	Pigment Yellow 3
11740	Pigment Yellow 65
11738	Pigment Yellow 73
11741	Pigment Yellow 74
11725	Pigment Orange 1
12310	Pigment Red 2
15865	Pigment Red 48
15800:2	Pigment Brown 5
15800	Pigment Red 64
Chemetron Corp., Pigments Div., Subsid. of Allegheny Ludlum Ind. Inc.	
11680	Pigment Yellow 1
11710	Pigment Yellow 3
11741	Pigment Yellow 74
12075	Pigment Orange 5
12120	Pigment Red 3
12085	Pigment Red 4
15865	Pigment Red 48
15630	Pigment Red 49
15860	Pigment Red 52
15585	Pigment Red 53
15880	Pigment Red 63
Harshaw Chemical Co.	
11000	Solvent Yellow 1
11680	Pigment Yellow 1
11710	Pigment Yellow 3
12705	Pigment Yellow 60
11740	Pigment Yellow 65
11738	Pigment Yellow 73
11741	Pigment Yellow 74
12075	Pigment Orange 5
12070	Pigment Red 1
12310	Pigment Red 2
12120	Pigment Red 3
12490	Pigment Red 5
12090	Pigment Red 6
12355	Pigment Red 23
15865	Pigment Red 48
15860	Pigment Red 52
15585	Pigment Red 53
14830:1	Pigment Red 54
14830	Acid Red 20
15850	Pigment Red 57
15880	Pigment Red 63
11855	Disperse Yellow 3
11110	Disperse Red 1
11215	Disperse Red 5
16105:1	Pigment Red 60:1
American Hoechst Corp. Industrial Chemicals Div.	
18852	Reactive Yellow 17
17757	Reactive Orange 16
11680	Pigment Yellow 1
11710	Pigment Yellow 3
11720	Pigment Yellow 9
11738	Pigment Yellow 73
11741	Pigment Yellow 74
11767	Pigment Yellow 97
12075	Pigment Orange 5
12367	Pigment Orange 38
12420	Pigment Red 7
12460	Pigment Red 9
12465	Pigment Red 15
12370	Pigment Red 112
12485	Pigment Red 146

Table 15 (Continued)

C.I. No.	C.I. Name
12475	Pigment Red 170
12467	Pigment Red 188
11077	Disperse Blue 165
11152	Disperse Brown 1
18097	Reactive Violet 5
Inmont Corp.	
12390	Pigment Red 17
15865	Pigment Red 48
15630	Pigment Red 49
15585	Pigment Red 53
15850	Pigment Red 57
15800:2	Pigment Brown 5
15800	Pigment Red 64
ICI Americas Inc.	
18967	Acid Yellow 19
17101	Acid Red 266
17053	Acid Red 57
--	Reactive Yellow 1
13190	Reactive Yellow 4
--	Reactive Orange 1
18158	Reactive Red 1
17908	Reactive Red 8
11152	Disperse Brown 1
18200	Reactive Red 2
18260	Reactive Orange 4
18270	Reactive Orange 13
Industrial Color, Inc.	
15630	Pigment Red 49
15585	Pigment Red 53
15850	Pigment Red 57
Indol Chemical Co., Inc.	
12355	Pigment Red 23
12320	Pigment Red 32

C.I. No.	C.I. Name
Keystone Color Works Inc.	
11680	Pigment Yellow 1
11730	Pigment Yellow 2
11710	Pigment Yellow 3
11660	Pigment Yellow 5
11727	Pigment Yellow 98
11725	Pigment Orange 1
12060	Pigment Orange 2
12070	Pigment Red 1
12310	Pigment Red 2
12120	Pigment Red 3
12090	Pigment Red 6
12395	Pigment Red 13
12315	Pigment Red 22
12355	Pigment Red 23
H. Kohnstamm & Co., Inc.	
17200	Acid Red 33
15985	Pigment Yellow 104
19140	Food Yellow 4
19140:1	Pigment Yellow 100
11680	Pigment Yellow 1
11710	Pigment Yellow 3
12705	Pigment Yellow 60
12120	Pigment Red 3
12085	Pigment Red 4
12090	Pigment Red 6
15630	Pigment Red 49
15585	Pigment Red 53
15850	Pigment Red 57
15880	Pigment Red 63
16105:1	Pigment Red 60:1
16035	Food Red 17

Table 15 (Continued)

C.I. No.	C.I. Name
Magruder Color Co.	
15865	Pigment Red 48
15860	Pigment Red 52
15585	Pigment Red 53
15850	Pigment Red 57
Max Marx Color & Chem. Co.	
19140	Food Yellow 4
19140:1	Pigment Yellow 100
12120	Pigment Red 3
12085	Pigment Red 4
12460	Pigment Red 9
12315	Pigment Red 22
15865	Pigment Red 48
15860	Pigment Red 52
15585	Pigment Red 53
16105:1	Pigment Red 60:1
Berncolors-Poughkeepsie Co.	
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
14710	Acid Red 4
14720	Acid Red 14
14025	Mordant Yellow 1
18821	Mordant Yellow 8
14110	Mordant Yellow 20
14030	Mordant Orange 1
18760	Mordant Red 7
15670	Mordant Violet 5
19555	Direct Yellow 28
13250	Mordant Brown 33
17590	Mordant Brown 40
13265	Mordant Brown 70

C.I. No.	C.I. Name
Passaic Color & Chem. Co.	
15970	Acid Orange 12
11160	Solvent Yellow 3
12055	Solvent Yellow 14
12700	Solvent Yellow 16
11021	Solvent Yellow 56
12100	Solvent Orange 2
12140	Solvent Orange 7
12150	Solvent Red 1
11320	Basic Orange 1
11320:1	Solvent Orange 4
11270	Basic Orange 2
11270:1	Solvent Orange 3
United Merchants & Manufacturers, Inc. Roma Chemical Div.	
12490	Pigment Red 5
12390	Pigment Red 17
12355	Pigment Red 23
12360	Pigment Red 31
15800:2	Pigment Brown 5
15800	Pigment Red 64
Sandoz, Inc., Colors & Chemicals Div.	
11680	Pigment Yellow 1
11765	Pigment Yellow 49
12310	Pigment Red 2
12490	Pigment Red 5
12420	Pigment Red 7
15865	Pigment Red 48
12475	Pigment Red 170
12480	Pigment Brown 1
Martin-Marietta Corp.	
11152	Disperse Brown 1

Table 15 (Continued)

Sterling Drug, Inc.
Hilton Davis Chemical Co. Div.

C.I. No.	C.I. Name
18965	Acid Yellow 17
15711	Acid Black 52
15985	Food Yellow 3
19140	Food Yellow 4
19140:1	Pigment Yellow 100
16105:1	Mordant Red 9
11680	Pigment Yellow 1
11741	Pigment Yellow 74
12075	Pigment Orange 5
12070	Pigment Red 1
12120	Pigment Red 3
12085	Pigment Red 4
12355	Pigment Red 23
12360	Pigment Red 31
15630	Pigment Red 49
15585	Pigment Red 53
15850	Pigment Red 57
16035	Food Red 17
16185	Acid Red 27

Sun Chemical Corp., Pigments Div.

C.I. No.	C.I. Name
11680	Pigment Yellow 1
11740	Pigment Yellow 65
11738	Pigment Yellow 73
11741	Pigment Yellow 74
12075	Pigment Orange 5
12120	Pigment Red 3
12390	Pigment Red 17
12315	Pigment Red 22
15865	Pigment Red 48
15630	Pigment Red 49
15860	Pigment Red 52
15585	Pigment Red 53
15850	Pigment Red 57
15880	Pigment Red 63
16105:1	Pigment Red 60:1

Stange Co.

C.I. No.	C.I. Name
15985	Food Yellow 3
19140	Food Yellow 4
19140:1	Pigment Yellow 100

Sterling Drug, Inc.,
Thomasset Colors Div.

C.I. No.	C.I. Name
15585	Pigment Red 53
15850	Pigment Red 57

Toms River Chemical Corp.

C.I. No.	C.I. Name
18965	Acid Yellow 17
18900	Acid Yellow 29
13065	Acid Yellow 36
19010	Acid Yellow 54
14170	Acid Yellow 65
13900	Acid Yellow 99
13900:1	Solvent Yellow 19
19005	Acid Yellow 127
13906	Acid Yellow 151
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
15575	Acid Orange 8
16230	Acid Orange 10
18732	Acid Orange 60
18745	Acid Orange 74
18050	Acid Red 1
14710	Acid Red 4
16255	Acid Red 18
17045	Acid Red 37
17053	Acid Red 57
17101	Acid Red 266
15620	Acid Red 88
17755	Acid Red 137
19351	Acid Red 179
16580	Acid Violet 3
14880	Acid Blue 158

Table 15 (Concluded)

C.I. No.	C.I. Name
13361	Acid Green 35
15711	Acid Black 52
18165	Acid Black 60
19140	Food Yellow 4
19140:1	Pigment Yellow 100
11320	Basic Orange 1
11320:1	Solvent Orange 4
11270	Basic Orange 2
11270:1	Solvent Orange 3
11055	Basic Red 22
11154	Basic Blue 41
--	Reactive Yellow 2
13245	Reactive Yellow 3
14030	Mordant Orange 1
19555	Direct Yellow 28
13250	Mordant Brown 33
14645	Mordant Black 11
15705	Mordant Black 17
11855	Disperse Yellow 3
11005	Disperse Orange 3
11227	Disperse Orange 25
11119	Disperse Orange 30
11110	Disperse Red 1
11210	Disperse Red 17
11228	Disperse Red 65
11116	Disperse Red 73
11152	Disperse Brown 1
14155	Direct Green 28
15050	Acid Blue 158:1
18950	Acid Yellow 40
17101	Acid Red 266
—	Acid Red 337
—	Disperse Blue 79

Paul Uhlrich & Co. Inc.

C.I. No.	C.I. Name
12060	Pigment Orange 2
12120	Pigment Red 3
12085	Pigment Red 4
12390	Pigment Red 17
12355	Pigment Red 23
15865	Pigment Red 48
15630	Pigment Red 49
15860	Pigment Red 52
15850	Pigment Red 57

Mobay Chemical Corp.
Verona Dyestuff Div.

C.I. No.	C.I. Name
13906	Acid Yellow 151
15510	Acid Orange 7
15510:1	Pigment Orange 17
15510:2	Pigment Orange 17:1
15510:3	Solvent Orange 49
15575	Acid Orange 8
18732	Acid Orange 60
18050	Acid Red 1
17755	Acid Red 137
12055	Solvent Yellow 14
11085	Basic Red 18
11741	Pigment Yellow 74
12770	Disperse Yellow 4
11227	Disperse Orange 25
11117	Disperse Red 90
11077	Disperse Blue 165
—	Acid Red 337

Warner-Jenkinson Co.

C.I. No.	C.I. Name
15985	Food Yellow 3
19140	Food Yellow 4
19140:1	Pigment Yellow 100
16035	Food Red 17
—	Disperse Blue 79

Cone Mills Corp.
Otto B. May Co. Div.

C.I. No.	C.I. Name
—	Disperse Blue 79

Table 16

PRODUCERS OF DISAZO DYES AND PIGMENTS

C.I. No.	C.I. Name
American Color & Chem. Co.	
20195	Acid Brown 14
20470	Acid Black 1
22240	Direct Blue 22
26077	Disperse Orange 29
26105	Solvent Red 24
26360	Acid Blue 113
26370	Acid Black 24
26410	Acid Blue 118
26900	Acid Red 151
26905	Acid Red 66
28160	Direct Red 81
29000	Direct Yellow 44
29025	Direct Yellow 50
29058	Direct Orange 72
29060	Direct Yellow 34
29156	Direct Orange 102
29160	Direct Red 23
29180	Direct Red 73
29185	Direct Red 24
29225	Direct Red 83
American Cyanamid Co.	
20170	Acid Orange 24
20177	Acid Brown 354
20195	Acid Brown 14
20470	Acid Black 1
21000	Basic Brown 1
21010	Basic Brown 4
24890	Direct Yellow 4
24895	Direct Yellow 12
26105	Solvent Red 24
26120	Solvent Red 26
26900	Acid Red 151
27290	Acid Red 73
28160	Direct Red 81
29156	Direct Orange 102
29160	Direct Red 23
Crompton & Knowles Corp., Dyes and Chemical Div.	
20170	Acid Orange 24
20195	Acid Brown 14
20470	Acid Black 1
26070	Disperse Yellow 23
26077	Disperse Orange 29
26360	Acid Blue 113
26900	Acid Red 151
27290	Acid Red 73
28160	Direct Red 81
29000	Direct Yellow 44
29025	Direct Yellow 50
29060	Direct Yellow 34
29065	Direct Red 79
29160	Direct Red 23
29185	Direct Red 24
29200	Direct Red 72
29225	Direct Red 83

Table 16 (Continued)

Atlantic Chemical Corp.

C.I. No.	C.I. Name
20110	Mordant Brown 1
20170	Acid Orange 24
20195	Acid Brown 14
20470	Acid Black 1
20495	Acid Green 20
24890	Direct Yellow 4
24895	Direct Yellow 12
25100	Mordant Yellow 16
25135	Acid Yellow 38
25380	Direct Red 75
26070	Disperse Yellow 23
26105	Solvent Red 24
26520	Mordant Orange 6
26900	Acid Red 151
27200/27201	Acid Red 115
27290	Acid Red 73
27680	Direct Red 16
27855	Direct Violet 7
27885	Direct Violet 9
27925	Direct Blue 67
28160	Direct Red 81
29100	Direct Red 31
29105	Direct Violet 14
29110	Direct Red 149
29120	Direct Violet 66
29156	Direct Orange 102
29160	Direct Red 23
29175	Direct Red 62
29185	Direct Red 24
29190	Direct Red 26
29200	Direct Red 72
29225	Direct Red 83

BASF Wyandotte Corp.

C.I. No.	C.I. Name
20170	Acid Orange 24
20195	Acid Brown 14
20470	Acid Black 1
21010	Basic Brown 4
21030	Basic Brown 2
21230	Solvent Yellow 29
21250	Solvent Red 22
24890	Direct Yellow 4
26077	Disperse Orange 29
26520	Mordant Orange 6
27290	Acid Red 73
28160	Direct Red 81
29156	Direct Orange 102
29200	Direct Red 72

Benzenoid Organics Inc.

C.I. No.	C.I. Name
20470	Acid Black 1
20495	Acid Green 20

E. I. du Pont de Nemours & Co., Inc.

C.I. No.	C.I. Name
21000	Basic Brown 1
24890	Direct Yellow 4
26900	Acid Red 151
28160	Direct Red 81
28255	Direct Orange 74
29156	Direct Orange 102
29160	Direct Red 23
29200	Direct Red 72

Eastman Kodak Co.

C.I. No.	C.I. Name
26070	Disperse Yellow 23

Table 16 (Continued)

C.I. No.	C.I. Name
Fabricolor Incorporated	
20170	Acid Orange 24
20470	Acid Black 1
29025	Direct Yellow 50
29030	Direct Yellow 51
29058	Direct Orange 72
29160	Direct Red 23
29185	Direct Red 24
29225	Direct Red 83
GAF Corp.	
21230	Solvent Yellow 29
American Hoechst Corp. Industrial Chemicals Div.	
20040	Pigment Yellow 16
20505	Reactive Black 5
ICI Americas Inc.	
26440	Reactive Brown 1
Keystone Color Works Inc.	
21010:2	Pigment Brown 3
H. Kohnstamm & Co., Inc.	
21010:2	Pigment Brown 3

C.I. No.	C.I. Name
C. Lever Co. Inc.	
24890	Direct Yellow 4
28160	Direct Red 81
Morton Norwich Products Inc.	
26050	Solvent Red 19
Berncolors-Poughkeepsie Co.	
20150	Mordant Brown 18
20460	Acid Blue 29
20470	Acid Black 1
20480	Acid Black 41
20495	Acid Green 20
26520	Mordant Orange 6
Passaic Color & Chem. Co.	
21000	Basic Brown 1
21010	Basic Brown 4
21010:1	Solvent Brown 12
21240	Solvent Yellow 30
26100	Solvent Red 23
26105	Solvent Red 24
26120	Solvent Red 26
26125	Solvent Red 27
27290	Acid Red 73
27291	Solvent Red 30
Martin-Marietta Corp.	
26077	Disperse Orange 29

Table 16 (Concluded)

Sterling Drug, Inc.
Hilton Davis Chemical Co. Div.

C.I. No.	C.I. Name
24890	Direct Yellow 4

Toms River Chemical Corp.

C.I. No.	C.I. Name
20110	Mordant Brown 1
20170	Acid Orange 24
20195	Acid Brown 14
20470	Acid Black 1
20495	Acid Green 20
21000	Basic Brown 1
21010	Basic Brown 4
24810	Acid Red 134
24890	Direct Yellow 4
24895	Direct Yellow 12
25200	Direct Orange 73
26070	Disperse Yellow 23
26520	Mordant Orange 6
26550	Acid Orange 51
26900	Acid Red 151
27290	Acid Red 73
27680	Direct Red 16
27885	Direct Violet 9
28160	Direct Red 81
29000	Direct Yellow 44
29025	Direct Yellow 50
29042	Direct Yellow 118
29058	Direct Orange 72
29060	Direct Yellow 34
29065	Direct Red 79
29100	Direct Red 31
29120	Direct Violet 66
29155	Direct Orange 29
29160	Direct Red 23
29165	Direct Red 4
29175	Direct Red 62
29185	Direct Red 24
29200	Direct Red 72
29210	Direct Red 122
29225	Direct Red 83

Mobay Chemical Corp.
Verona Dyestuff Div.

C.I. No.	C.I. Name
20250	Acid Brown 83
26077	Disperse Orange 29
26900	Acid Red 151

4

Table 17

PRODUCERS OF TRISAZO, TETRAKIS, AND POLYAZO DYES AND PIGMENTS

C.I. No.	C.I. Name
American Color & Chemical Corp.	
30015	Direct Black 78
31600	Direct Black 80
34085	Direct Blue 120
34090	Direct Blue 120A
34200	Direct Blue 78
35435	Direct Black 22
35780	Direct Red 80
Crompton & Knowles Corp., Dyes and Chemical Div.	
31600	Direct Black 80
35435	Direct Black 22
35780	Direct Red 80
Atlantic Chemical Corporation	
31600	Direct Black 80
34010	Direct Blue 126
35435	Direct Black 22
35780	Direct Red 80

C.I. No.	C.I. Name
Fabricolor Incorporated	
31600	Direct Black 80
35005	Direct Brown 44
35780	Direct Red 80
Toms River Chemical Corp.	
34045	Direct Green 26
34085	Direct Blue 120
34090	Direct Blue 120A
34260	Direct Green 51
35255	Direct Black 19
35435	Direct Black 22
35780	Direct Red 80
Mobay Chemical Corp. Verona Dyestuff Div.	
35435	Direct Black 22

Table 18

PRODUCERS OF AZOIC DIAZO COMPONENTS

C.I. No.	Azoic Diazo Component
Synalloy Corp., Blackman-Uhler Chemical Div.	
37010	3
37040	9
37050	49
37105	12
37110	8
37120	10
37125	5
37130	13
37135	1
Atlantic Chemical Corp.	
37000	44
37120	10
37175	20
E.I. du Pont de Nemours & Co., Inc.	
37040	9
37125	5
37135	1

C.I. No.	Azoic Diazo Component
Alliance Chemical Corp.	
37000	44
37010	3
37025	6
37040	9
37050	49
37085	11
37090	32
37100	34
37110	8
37120	10
37125	5
37130	13
37135	1
37150	42
37151	14

Table 19

PRODUCERS OF AZOIC COUPLING COMPONENTS

C.I. No.	Azoic Coupling Component
Pfister Chemical Works	
37505	2
37510	10
37515	17
37525	8
37526	21
37527	29
37530	20
37531	34
37545	19
37550	12
37558	14
37565	7
37615	35

C.I. No.	Azoic Coupling Component
Synalloy Corp., Blackman-Uhler Chemical Div.	
37520	18
37526	21
37527	29
37530	20
37531	34
37558	14
37565	7
37600	15
--	43
Alliance Chemical Corp.	
--	43

Table 20

ESTIMATED TOTAL QUANTITY OF ORGANIC INTERMEDIATES IN SOLID AND AQUEOUS-SOLID WASTES FROM THE MANUFACTURE OF AZO DYES AND PIGMENTS OTHER THAN THOSE BASED ON BENZIDINE AND ITS CONGENERS

Intermediate	Solid Residues (kg/yr)	Aqueous Solid Wastes (kg/yr)
2-Naphthol	2430	204000
3-Hydroxy-2-naphthoic acid	1320	109000
2-Amino-1-naphthalene sulfonic acid	1190	--
2-Amino-5-chloro-p-toluene sulfonic acid	975	--
6-Amino-m-toluene sulfonic acid	580	--
2-Hydroxy-6-naphthalene sulfonic acid	510	42200
2-Bromo-4,6-dinitroaniline	480	--
m-Diethanolamino-p-methoxy-acetanilide	480	39800
4-Aminobenzene sulfonic acid	450	96
6-Amino-4-chloro-m-toluene sulfonic acid	430	--
Acetoacetanilide	350	40400
o-Acetoacetanisidide	330	27400
4-Amino-5-methoxy-o-toluene sulfonic acid	325	--
2-Amino-1-phenol-4-sulfonamide	320	--
Aniline	310	710
p-(p-Aminophenylazo)benzene sulfonic acid	270	--
p-Nitroaniline	270	--

Table 20 (Continued)

Intermediate	Solid Residues (kg/yr)	Aqueous Solid Wastes (kg/yr)
N-Benzoyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	270	22400
2-Nitro-p-toluidine	260	--
Phenol	235	19200
4-Nitro-o-anisidine	220	--
6-Amino-4-hydroxy-2-naphthalene sulfonic acid	203	17400
α,α,α-Trifluoro-o-toluidine	200	--
3-Carboxy-1-(p-sulfophenyl)-5-pyrazolone	180	15300
3-(N-Ethylanilino) propionitrile	120	10200
4-Chloro-2-nitroaniline	120	--
2,4-Dinitroaniline	120	--
6,6'-Ureylenebis-1-naphthol-3-sulfonic acid	115	14700
2-Chloro-4-nitroaniline	110	--
p-Phenylazoaniline	100	--
o-Anisidine	100	140
m-Phenylenediamine	98	6500
2,4-Diaminotoluene	80	1980
5-Nitro-o-anisidine	75	--
3-Hydroxy-3'-nitro-2-naphthanilide	75	6230
2-(N-Ethylanilino) ethanol	70	5600
1-Amino-2-hydroxy-6-nitro-4-naphthalene sulfonic acid	70	--

Table 20 (Concluded)

Intermediate	Solid Residues (kg/yr)	Aqueous Solid Wastes (kg/yr)
N-Acetyl-2-amino-5-hydroxy-7-naphthalene sulfonic acid	60	880
1-Amino-4-naphthalene sulfonic acid	60	50
3-Methyl-1-phenyl-5-pyrazolone	60	6900
p-Aminoacetanilide	60	--
2-Hydroxy-3,6-naphthalene disulfonic acid	55	4530
2-Aminobenzene carboxylic acid	55	--
4,4'-Diamino-2,2'-stilbene disulfonic acid	50	--
6-Amino-3,4'-azodibenzene sulfonic acid	50	--

REFERENCES

Abrahart, E. N. 1968. Dyes and Their Intermediates. Pergamon Press, New York.

ADMI (American Dye Manufacturers Institute, Inc.). 1973. Dyes and the Environment, Vol 1.

Anliker, R., and E. A. Clarke, 1979. The Ecology and Toxicology of Synthetic Organic Pigments. Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry, Clara Strasse 4/6, P.O. Box CH-4005, Basel, Switzerland.

Baird, R., L. Carmona, and R. L. Jenkins. 1977. Behavior of Benzidine and Other Aromatic Amines in Aerobic Wastewater Treatment. Journal of the Water Pollution Control Federation 49:1609-1615.

BIOS (British Intelligence Objectives Subcommittee). 1945. German Dyestuffs and Dyestuffs Intermediates, Azo and Lake Dyestuffs. BIOS Final Report No. 961, Item No. 22. H. M. Stationery Office, London.

Boeniger, M. 1980. Carcinogenicity and Metabolism of Azo Dyes, Especially Those Derived from Benzidine. Technical Report DHHS 80-119. US Department of Health and Human Services, National Institute of Occupational Safety and Health, Cincinnati, Ohio.

Brown, D., H. R. Hitz, and L. Schafer. 1981. Chemosphere 10(5):245-261.

The Society of Dyers and Colourists. 1980. Colour Index Lund Humphries Printers, London, England, Volumes 1-3, third edition, 1971 Volume 6, revised third edition, 1975; additions and amendments numbers 13-16, October 1974-July 1980.

Crossley, Kienle, and Benbrook. 1940. JACS 62:1400.

DETO (Dyes Environmental and Toxicology Organization, Inc.), New York. 1980. Comments on the Testing Recommendations of the TOSCA Interagency Testing Committee for Benzidine-based Dyes.

Dieckhues, B. 1961. Experiments on the Reductive Splitting of Azo Dyes by Bacteria. Zentbl. Bakt. Parasitkde 180:244-249.

Dubin, P., and K. L. Wright. 1975. Reduction of Azo Dyes in Cultures of Proteus Vulgaris, Zenobiotica 5:563-571.

EPA (U. S. Environmental Protection Agency). 1975. Development Document, Significant Organic Products of Organic Chemical Manufacturing. EPA-440/1-75-045. U.S. Environmental Protection Agency, Washington, D.C.

Flege, R. K. 1970. Determination of Degraded Dyes and Auxiliary Chemicals in Effluents from Textile Dyeing Processes. Georgia Institute of Technology, Atlanta, Georgia.

Games, L. M., and R. A. Hites. 1977. Analytical Chemistry 49:1433-1440.

Hansch, C. 1978. Pomona College Data System, Seaver Chemistry Laboratory, Pomona College.

Hanson, J. B. 1979. Development Document for Existing Source Pretreatment Standards for the Electroplating Point Source Category, EPA 440/1-79/003, U. S. Environmental Protection Agency, Effluent Guidelines Division, Washington, D.C.

Hitz, H. R., W. Huber, and R. H. Reed. 1978. The Adsorption of Dyes on Activated Sludge. Journal of the Society of Dyers and Colourists 94:71-76.

Hughes, E. C., C. K. Ingold, and J. H. Ridd. 1958. Journal of the Chemical Society (London) 1958:58, 65, 70, 77, 82, 86.

Idaka, E., et al. 1978. Degradation of Azo Compounds by *Aeromonas hydrophila* var. 24B. Journal of the Society of Dyers and Colourists. March 1978. pp. 91-94.

Kappeler, T., et al. 1978. Are Azo Dyes Degradable? Textile Chemist and Colourist 10:10.

Kenaga, E. E., and C. A. I. Goring. 1978. Relationship Between Water Solubility, Soil-Sorption, Octanol-Water Partitioning, and Bioconcentration of Chemicals in Biota. Preprint of paper given at ASTM 3rd Aquatic Toxicol. Symp., October 17-18, 1978, New Orleans, Louisiana.

Keinath, T. M. 1976. Benzidine: Wastewater Treatment Technology. EPA-440/9-76-018. U.S. Environmental Protection Agency, Washington, D.C.

Kent, J. A., Editor. 1974. Riegel's Handbook of Industrial Chemistry, 2nd Edition. Van Nostrand Reinhold Company, New York.

Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition. 1978. 3:772-777. John Wiley and Sons, Inc., New York.

Lapp, T. W., et al. 1979. A Preliminary Materials Balance for Dyes and Pigments from Benzidine and Three Benzidine Derivatives. Midwest Research Institute Draft Report. U. S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Lubs, H. A. 1955. The Chemistry of Synthetic Dyes and Pigments. American Chemical Society Monograph No. 127. Van Nostrand Reinhold Company, New York. p. 101.

Mabey, W. R. et al., 1981. Aquatic Fate Process Data for Organic Priority Pollutants EPA 68-0003-2981. U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington, D.C.

Melnikov, B. N., and M. N. Kirillova. 1969. Thermal Stability of Direct Dyes in Solution. Zhurnal Prikladnoi Khimii 42.

Meyer, U., et al. 1979. The Biologic Degradation of 1920 Azo Dyes. Textilveredlung 14:15-20.

Mill, T., et al. 1980. Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Athens, Georgia.

Patterson, J. W., and R. A. Minear. 1971. Wastewater Treatment Technology, Illinois Institute for Environmental Quality, Chicago, Illinois.

Peck, K., and J. C. Gorton, Jr. 1977. Industrial Waste Pretreatment in the Buffalo Minicipal System EPA 600/2-77-018. U. S. Environmental Protection Agency, Office of Research and Development, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma.

Porter, J. J. 1973. Stability and Removal of Commercial Dyes from Process Wastewater. Pollution Engineering. October 1973. pp. 27-30.

Roberts, J. D., and M. C. Caserio. 1964. Basic Principles of Organic Chemistry. W. A. Benjamin, Inc., New York.

Rys, P., and H. Zollinger. 1972. Fundamentals of the Chemistry and Application of Dyes. John Wiley and Sons, Inc., New York.

Saunders and Waters. J. C. S. 1154 (1946).

Shreve;, R. N., and J. A. Brink. 1977. Chemical Process Industries, 4th ed. McGraw-Hill Book Company, New York.

Smith, J. H., W. R. Mabey, N. Bohonos, B. R. Holt, S. S. Lee, T. W. Chou, D. C. Bomberger, and T. Mill. 1977. Environmental Pathways of Selected Chemicals in Freshwater Systems. Part I: Background and experimental Procedures, U.S. Environmental Protection Agency. EPA-600-7-77-113.

Smith, J. H., W. R. Mabey, N. Bohonos, B. R. Holt, S. S. Lee, T. W. Chou, D. C. Bomberger, and T. Mill. 1978. Environmental Pathways of Selected Chemicals in Freshwater Systems. Part II: Laboratory Studies. U.S. Environmental Protection Agency, Off. Res. Dev., EPA-600/7-78-074.

Snow. 1932, Ind. Eng. Chem. 24:1420.

Steadman, T. R., et al. 1977. Industrial Process Profiles for Environmental Use; Chapter 7, Organic Dyes and Pigments Industry. EPA 600/2-77-023g. U. S. Environmental Protection Agency, Washington, D.C.

Swett, L., A. Twhigg, and K. E. McCaleb. 1983. The Organic Dyes and Pigments Data Base. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio. Contract No. 68-03-2944.

APPENDIX A

EXAMPLE OF MULTISTAGE PROCESS FOR A COMPLEX AZO DYE

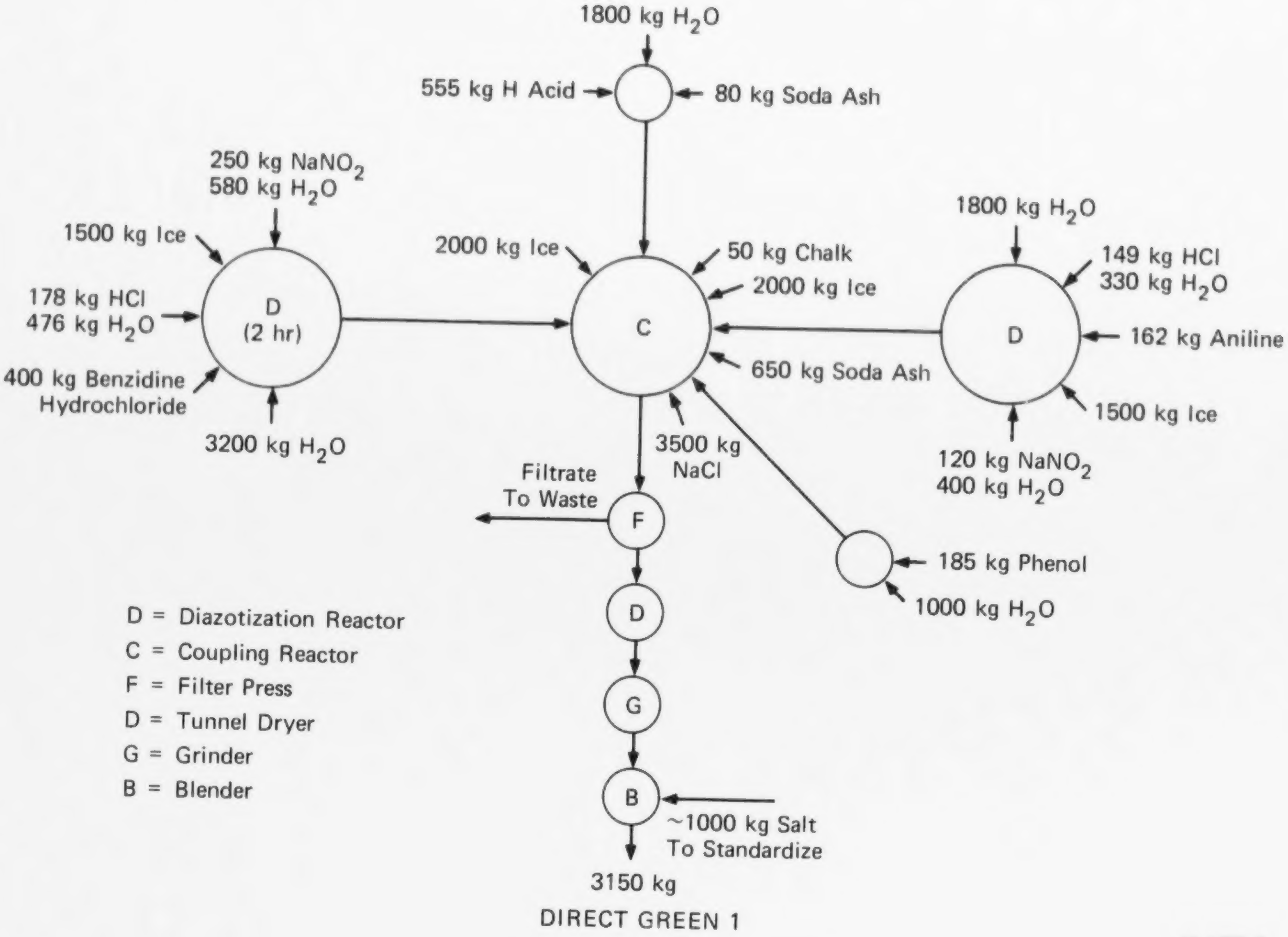
For many azo dyes, two or three stages of diazotization and coupling are required. Other types of reactions may also be required for these dyes, and they are performed in either the coupling or diazotization reactors. An intricate piping system is provided to interconnect the various diazotization and coupling reactors, and the filter presses. Some recipes call for the clarification of certain solutions or reaction intermediates, and clarifying filters are provided for this.

As an example of the processes used for manufacturing most of the azo dyes and pigments, Figure A-1 shows the steps necessary for producing one complex azo dye--Direct Green 1 (Colour Index No. 30280) based on benzidine. This benzidine example is used because the description was already available from a previous report that considered azo dyes and pigments produced from benzidine and its congeners separately because they were perceived to be especially hazardous.

The synthesis consists of two diazotizations and three coupling reactions involving four organics: a diamine(benzidine), H acid, aniline, and phenol. The ingredients are added at each stage in the clockwise order of the arrows. The diamine is converted to the tetrazonium salt, H acid is coupled to one diazonium group on the diamine, aniline is diazotized and coupled to the H acid, and finally phenol is coupled to the other diazonium group remaining on the diamine. Figure A-2 shows the representative chemical reactions at each step, assuming that the reactions are complete and no by-products are formed.

The detailed recipe for producing Direct Green 1, which was adapted from the BIOS (1945) reports, is as follows:

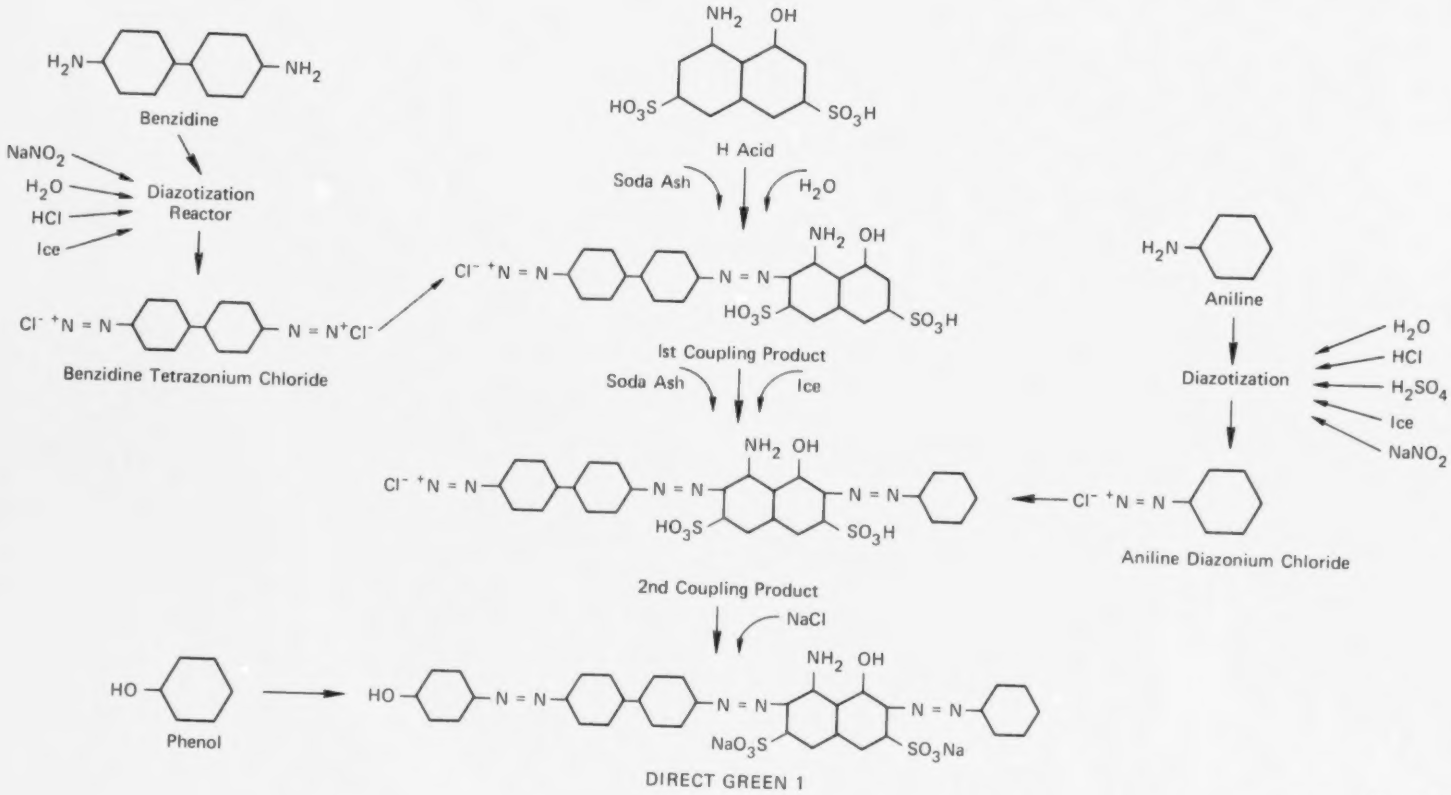
> Stir 400 kg benzidine hydrochloride in 3,200 liters water in a diazotization reactor, add 500 liters 30% hydrochloric acid, and stir overnight. Cool to 0^{o}C with 1,500 kg ice; add 250 kg sodium nitrite as a 30% solution (temp 0^{o}-4^{o}C, volume 5,000 liters). Diazotization should be complete in two hours.
>
> For the first coupling (on the acid side), transfer to a 12,000-liter vessel containing 1,500-2,000 kg ice. Stir 555 kg H acid into 1,800 liters water at 40^{o}C and dissolve (by dusting in) 80 kg soda ash (volume 2,500-3,000 liters). Run the H acid into the tetrazonium salt over two hours with rapid stirring (temp 0^{o}C, volume 9,000 liters). Stir slowly


1800 kg H_2O
555 kg H Acid
80 kg Soda Ash
250 kg $NaNO_2$
580 kg H_2O
1500 kg Ice
178 kg HCl
476 kg H_2O
D
(2 hr)
400 kg Benzidine Hydrochloride
3200 kg H_2O
2000 kg Ice
C
50 kg Chalk
2000 kg Ice
650 kg Soda Ash
3500 kg NaCl
1800 kg H_2O
149 kg HCl
330 kg H_2O
D
162 kg Aniline
1500 kg Ice
120 kg $NaNO_2$
400 kg H_2O
185 kg Phenol
1000 kg H_2O
Filtrate To Waste
F
D
G
B
~1000 kg Salt To Standardize
3150 kg
DIRECT GREEN 1
D = Diazotization Reactor
C = Coupling Reactor
F = Filter Press
D = Tunnel Dryer
G = Grinder
B = Blender

JA-1706-2

FIGURE A-1 STEPS REQUIRED FOR PRODUCTION OF DIRECT GREEN 1

(Components added in clockwise order.)


Benzidine
NaNO$_2$
H$_2$O
HCl
Ice
Diazotization Reactor
Benzidine Tetrazonium Chloride
H Acid
Soda Ash
H$_2$O
Ist Coupling Product
Soda Ash
Ice
Aniline
Diazotization
H$_2$O
HCl
H$_2$SO$_4$
Ice
NaNO$_2$
Aniline Diazonium Chloride
2nd Coupling Product
NaCl
Phenol
DIRECT GREEN 1

JA-1706-3

FIGURE A-2 REPRESENTATIVE CHEMICAL REACTIONS IN THE MANUFACTURE OF DIRECT GREEN 1 for three hours, then add slowly 25 kg powdered chalk and later that night 25 kg more. The next day the batch should have a slight excess of H acid. Add more chalk if the coupling is not complete. Run into a 30,000-liter coupling vessel.

In a diazotization reactor, dissolve 162 kg aniline in 1,800 liters water with 420 liters 30% hydrochloric acid or 310 liters 40°Be sulfuric acid; add 1,500 kg ice. Diazotize at 0°C by adding 120 kg sodium nitrite as a 30% solution (volume 3,500 liters). In a separate reactor dissolve 185 kg phenol in 1,000 liters water at 70°C by adding 100 liters 50% caustic soda solution.

Add 2,000 kg ice to the first coupling product, then add the aniline diazonium salt, then, immediately and as rapidly as possible, add 650 kg solid soda ash, keeping the batch at 0°C. After two hours, the aniline diazonium salt should be gone, or almost so. Then add the phenol solution. The batch gets very thick and the stirring may have to be stopped. Allow to stand overnight to complete the reaction and permit Crystal growth. Next morning heat to 65°C with direct steam, add 3,500 kg salt, stir two hours while cooling to 50°C, and filter. The filtrate should be a pale blue-black color. Dry at 95°C, grind, and standardize with salt in a blender.

Yield is about 2,000 kg, before standardization. After blending, a typical final product yield is 3150 kg.

APPENDIX B

ESTIMATION OF BY-PRODUCTS AND UNREACTED INTERMEDIATES PRODUCED BY DYE AND PIGMENT MANUFACTURE

It is not possible to calculate the amounts of by-products and unreacted intermediates that are produced for each dye and pigment. Recipes reflecting current practice are not available, and rates for conversion to the numerous possible by-products have not been determined. A procedure was developed to obtain order of magnitude estimates of the amounts of unreacted intermediates and by-products that might be present in the reaction mixture after all of the coupling reactions were completed. The final result was a set of emission factors for these dyes and pigments that expressed the amount of unreacted intermediate and by-product in the final reaction mixture (the mother liquor) as a percentage of the final standardized product. These emission factors can be used to estimate the amounts of unreacted intermediate and by-product produced without working out in detail the stoichiometry of all of the dyes and pigments included in this study. Several assumptions were required. It was assumed that each coupling component was added to the reaction at a 5% molar excess with respect to the diazo component. It was also assumed that during each coupling reaction 5% of the diazonium salt present in the vessel decomposes and terminates. Production of other by-products such as miscouplings, was estimated and included in an overall by-product estimate. It was assumed that the diazotization reactions are complete.

The consequences of these assumptions are worked out in Table B-1, for Acid Black 1. It is made by first coupling diazotized p-nitroaniline (component A) to H acid (component C) under acid conditions and then coupling diazotized aniline (component A') to the monoazo product under alkaline conditions.

The three starting materials are added on a 1 molar basis with a 5% excess for the coupling component H acid. After the first coupling, only traces of the diazotized p-nitroaniline are expected. The monoazo product is assumed to account for 95% of the initial p-nitroaniline charge of 1 mole, which leaves 5% as the terminated p-nitroaniline by-product (assumed to be p-chloronitrobenzene). The coupling component, which was added in 0.05 molar excess, is estimated to be 0.1 molar excess after the first coupling reaction because 0.05 mole of the diazo compound did not react (1.05 moles of H acid was added but only 0.95 was estimated to be in the monoazo product, leaving 0.1 mole of unreacted intermediate). The second coupling reaction is assumed to yield 0.9 mole of the disazo product (95% or 0.90 mole). This means that 0.1 mole of diazotized aniline must either terminate or react with the free H acid remaining after the first coupling reaction. For consistency, 0.05 mole

Table B-1

EXAMPLE ESTIMATION OF BY-PRODUCTS AND UNREACTED INTERMEDIATES FROM PRODUCTION OF ACID BLACK 1

Material	Weight (kg-mole)	Weight (kg)
Starting materials		
p-Nitroaniline (A)	1.0	138
H acid (C)	1.05	335
Aniline (A')	1.0	93
Compounds after first coupling		
p-Nitroaniline (A)	Trace	--
H acid (C)	0.1	36
Monoazo product (A-C)	0.95	488
By-products (terminated A)	0.05	8
Compounds after second coupling		
p-Nitroaniline (A)	Trace	--
H acid (C)	0.05	18
Aniline (A')	Trace	--
Disazo product (A-C-A')	0.90	554
By-products	0.20	61

Organic dye yield	554
Total unreacted intermediates	18
Total by-products	61

of diazotized aniline was assumed to terminate (to phenol), and 0.05 mole was assumed to couple to free H acid giving a monoazo by-product. The remaining by-product could be 0.05 mole of the monoazo product from the first coupling reaction. This gives the total estimated by-product formation as 0.2 mole. The net results are 18 kg of unreacted intermediates (3.2% of the organic dye yield) and 61 kg of by-products (11% of the organic dye yield).

In a similar manner, the by-product formation was estimated for several dyes and pigments from each azo subclass (monoazo, Disazo I, Disazo II, and so forth). The compounds chosen were among the large volume dyes and pigments included in this study, namely:

Monoazo

- Pigment Red 49
- Pigment Red 53
- Pigment Red 57
- Acid Yellow 151

Disazo

- Acid Black 1
- Direct Yellow 4
- Direct Red 81
- Direct Yellow 50

Trisazo

- Direct Black 78
- Direct Black 80
- Direct Blue 126

Tetrakisazo

- Direct Black 22
- Direct Black 19

Although some variation in by-product formation may occur between these subgroupings, it was assumed that the estimates could be averaged for each major subclass. The results of this analysis is shown in Table B-2. The by-product production is estimated to double with each added azo bond. The tetrakis and polyazo compounds could be expected to have high amounts of impurities, whereas the monoazo compounds should be relatively pure. The unreacted intermediates remaining after completed dye synthesis represent about 4 wt% of the pure dye product for all azo dye and pigment subclasses.

Table B-2

RESULTS OF BY-PRODUCT ESTIMATION FROM AZO DYE SYNTHESIS
(% dye product as pure color)

Azo Dye Subclass	Average wt% By-Product	Average wt% Unreacted Intermediates
Monoazo	3	5
Disazo	8	4
Trisazo	15	4
Tetrakisazo	30	4

The condensation, esterification, and premetallization reactions are discussed in Section 3. The completeness of these reactions and the by-products formed are discussed below.

Condensation Reactions with Cyanuric Chloride

The conditions for reaction of an amine with cyanuric chloride together with the high reactivity of cyanuric chloride are assumed to lead to nearly complete reaction with few degradation by-products. The major source of by-products will be from the condensation of cyanuric chloride with the by-products and excess intermediates remaining from previous coupling reactions.

A 100% yield was assumed for each condensation reaction with cyanuric chloride, and, because of the high reactivity of cyanuric chloride, no unreacted material was assumed to remain. The unreacted intermediate release estimate, due to previous reactions, was reassigned to the by-product category since any unreacted amine intermediates would be condensed with cyanuric chloride to produce by-products.

Premetallized Dyes

The conditions used to premetallize a dye are such that the metallization reaction is essentially complete. The unreacted intermediates will not react to form a metal complex but certain monoazo by-products (in the poly azo dye categories) may metallize along with the dye. A majority of the premetallized dyes included in this study belong to the monoazo class; thus it was assumed that no by-products are formed from the metallization reaction.

Esterification Reactions

Esterification reactions are specific and under the conditions used in azo dye manufacture should not produce significant amounts of by-products; therefore it was assumed that no excess esterifying compound was required. Since the esterifying compound is added on a molar basis with respect to the diazonium starting material, it will be in excess because of incomplete coupling reactions. The by-products that will occur are the condensation products of the esterifying compound with any excess coupling component or by-product from previous reaction steps that carry free hydroxyl groups. The unreacted intermediate release estimate from the previous coupling is reassigned to the by-product category to account for this effect. The esterifying reactions were assumed to be complete giving 100% yield.

Phosgenation Reactions

Because the degradation product of an isocyanate is the parent amine, no by-products are expected to occur from this reaction step. The procedure for the reaction calls for the addition of phosgene until no residual amine is detected. From the above considerations, it was assumed that the phosgenation reaction was complete and led to no by-products. The by-products that will arise, however, are from the phosgenated unreacted intermediates and by-products from previous coupling reactions.